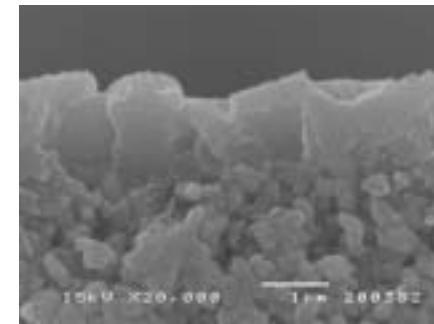
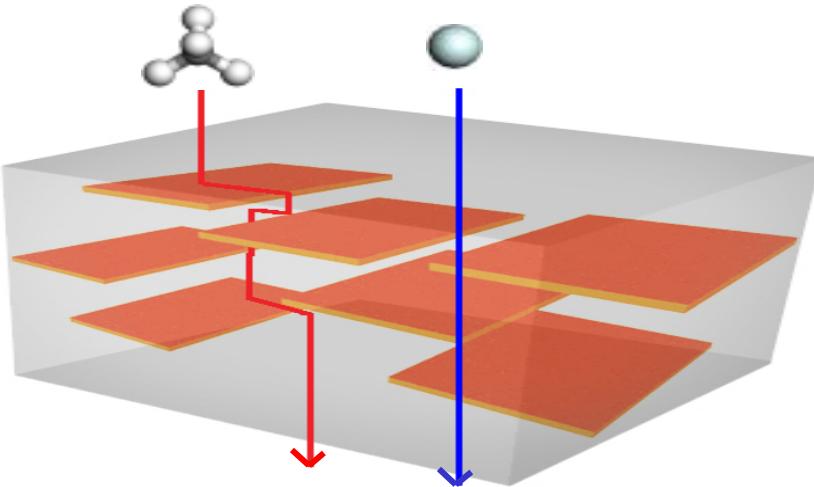


August 17, 2004
Workshop on Membrane Science
Argonne National Lab

Molecular Sieve Films

and

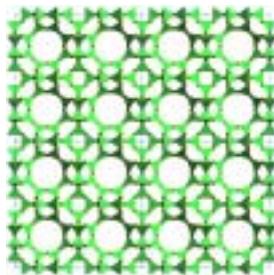


Polymer-Selective-Flake Nanocomposites

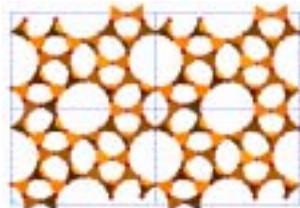
Molecular Sieve Films

Zeolites

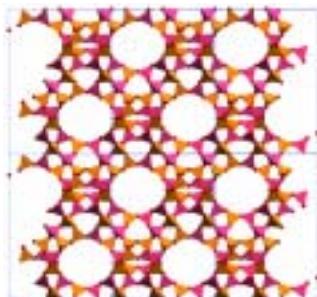
LTA



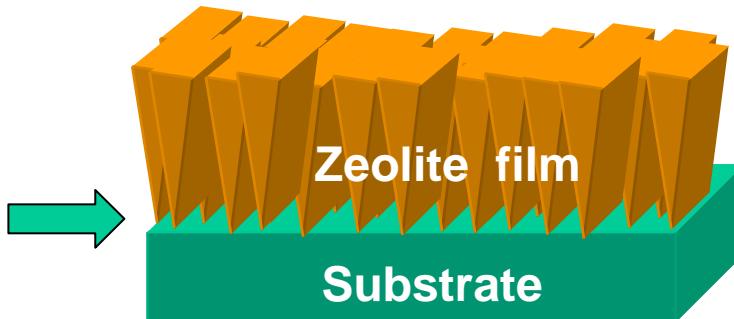
MFI



FAU



Supported Zeolite membranes



- High selectivity
- High thermal and chemical stability

Applications

Corrosion Protection layers
(Yan Y., ...)

Separation membranes
(Hedlund J., ...)

Catalytic membranes
(Santamaria J., ...)

Chemical Sensors
(Bein T., ...)

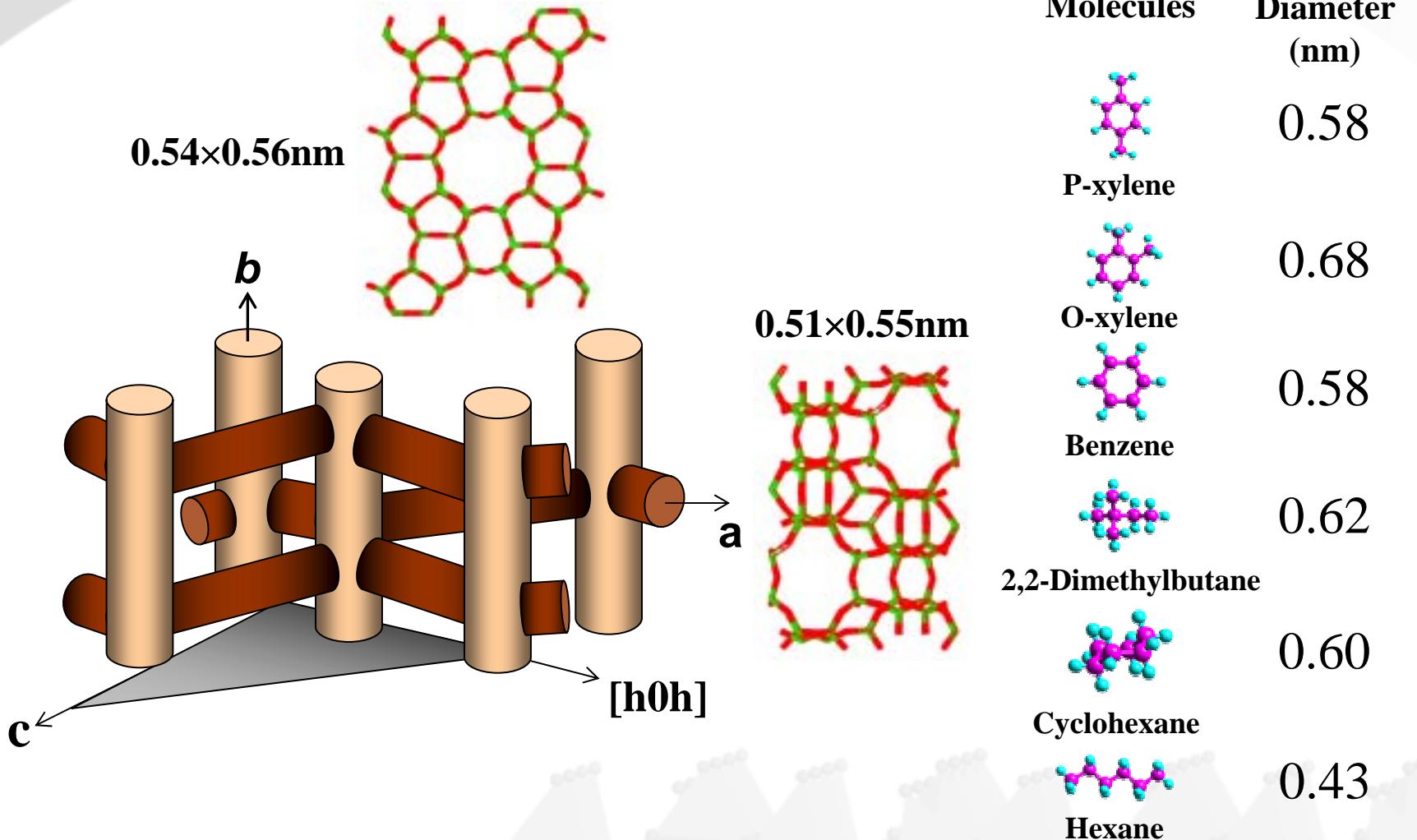
Insulation layers
(Yan Y., ...)

Thermoelectric Devices
(Hillhouse)

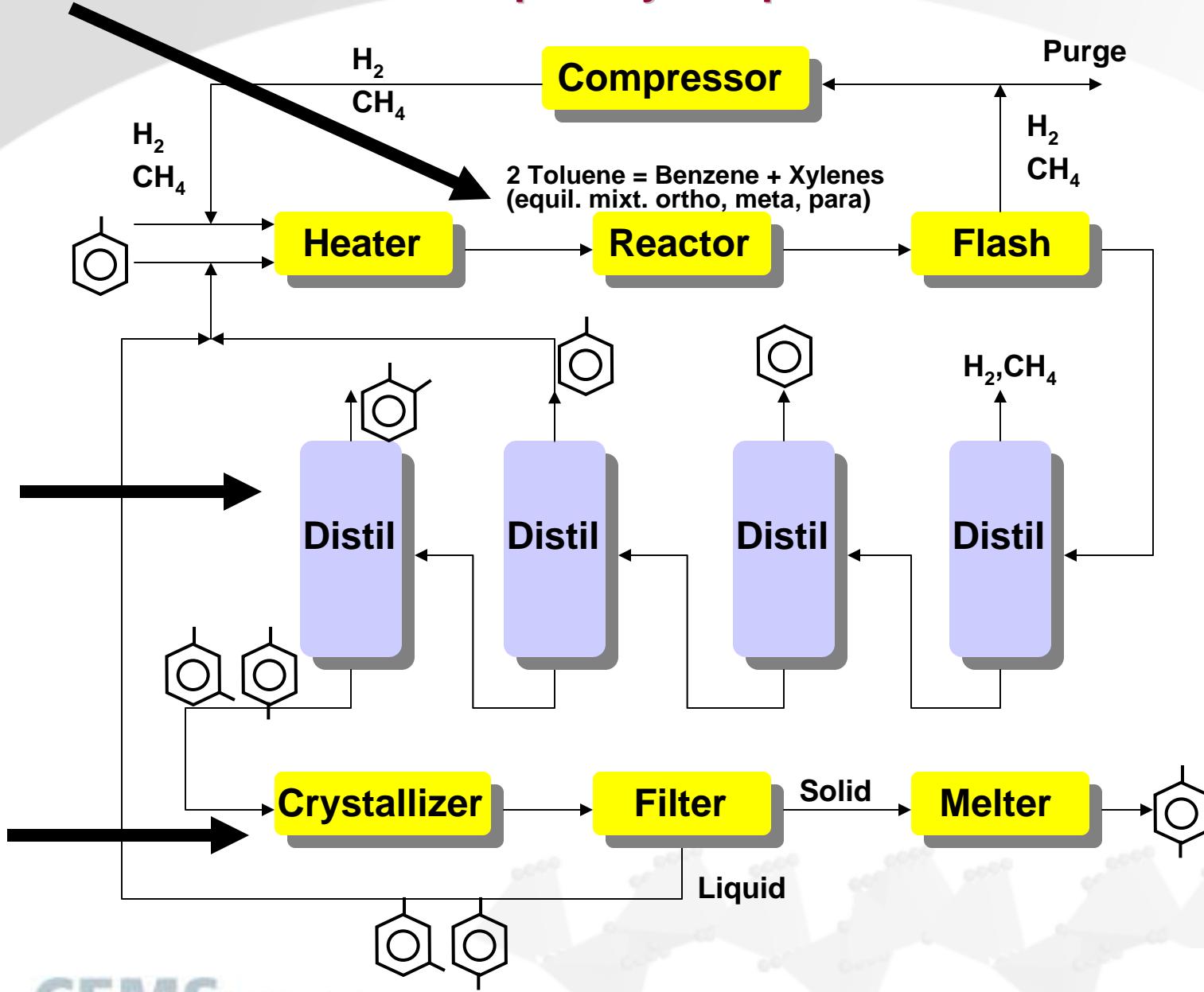
Nano-
technology



The Pore Structure of MFI type of Zeolites (ZSM-5 & Silicalite-1)

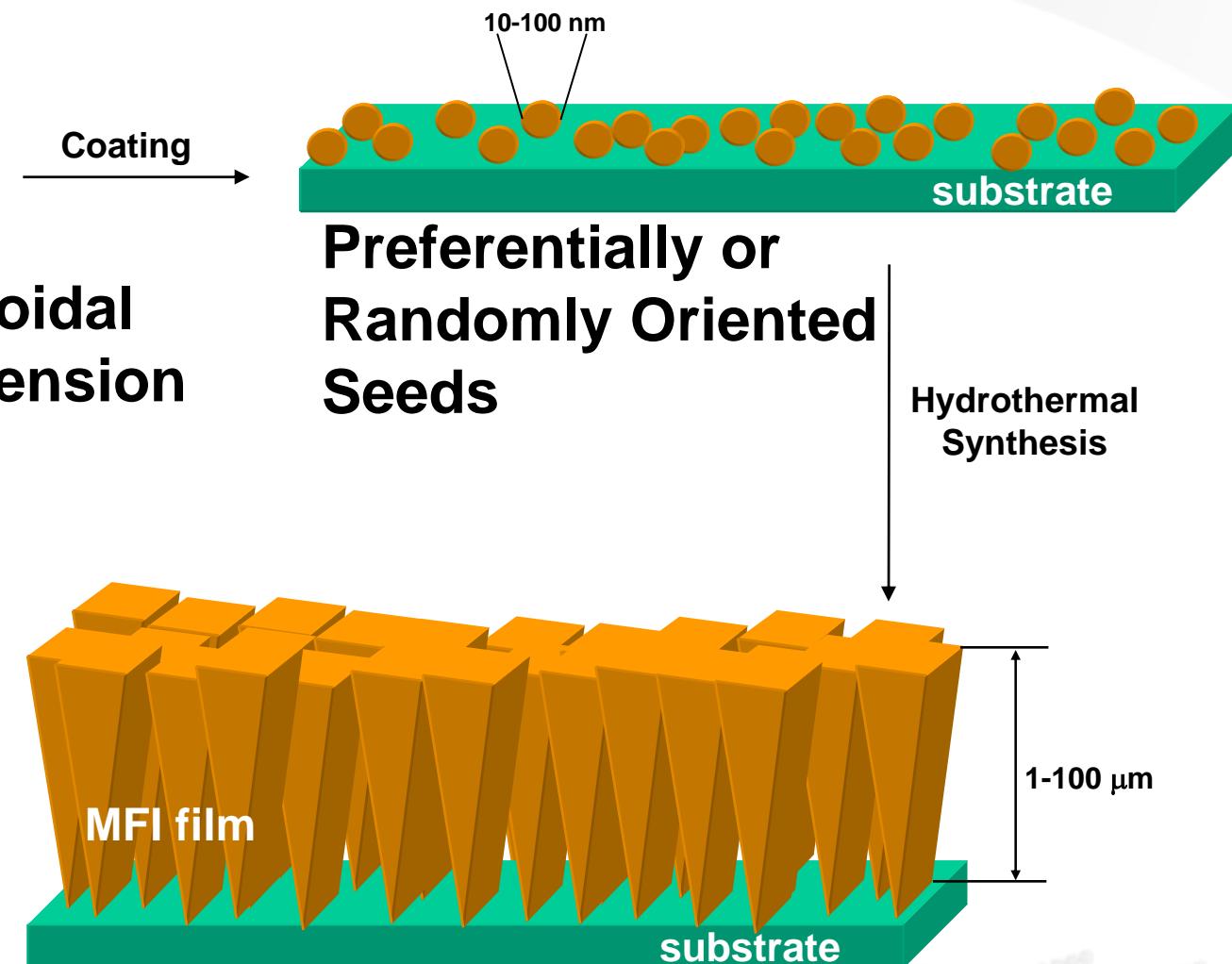


para-xylene plant

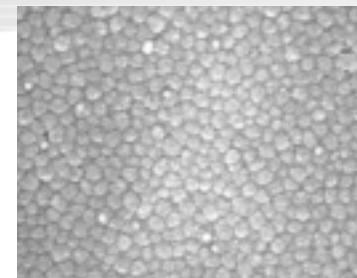
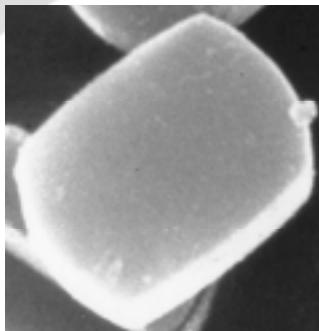




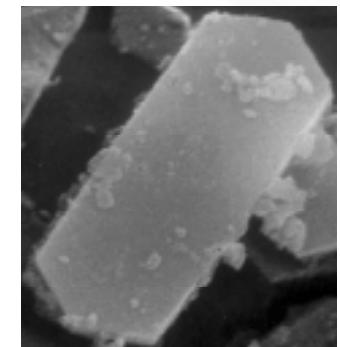
**Colloidal
Suspension**



1 μ m

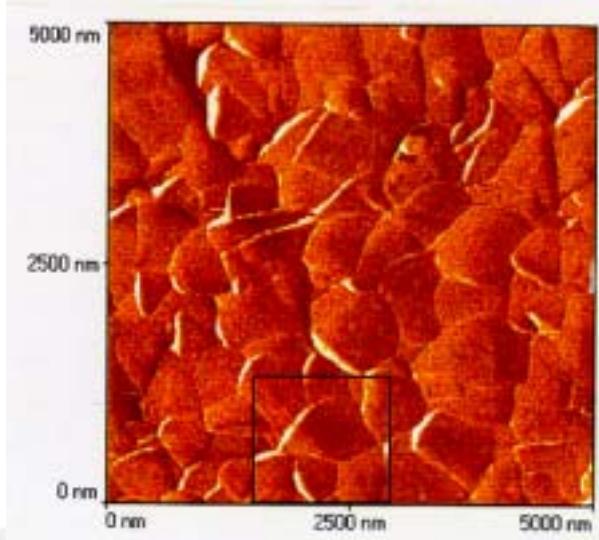
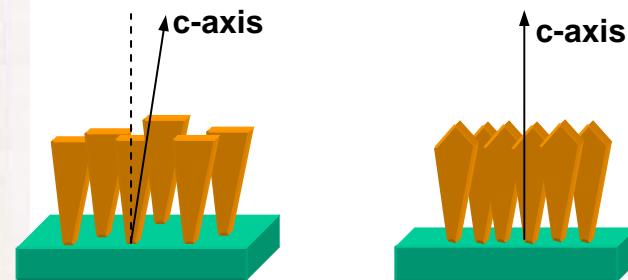
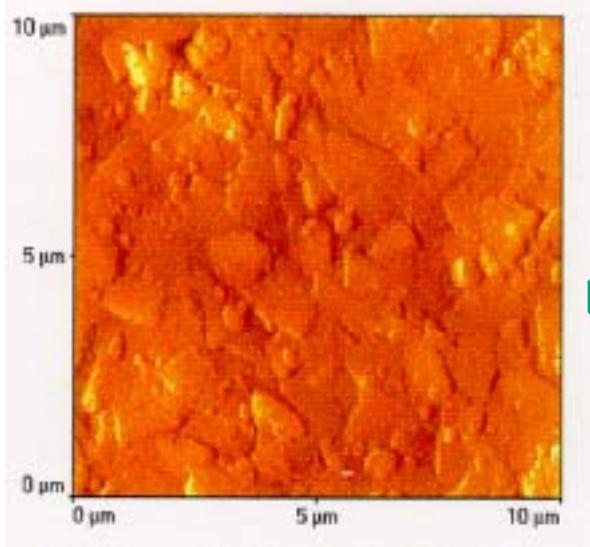


1 μ m



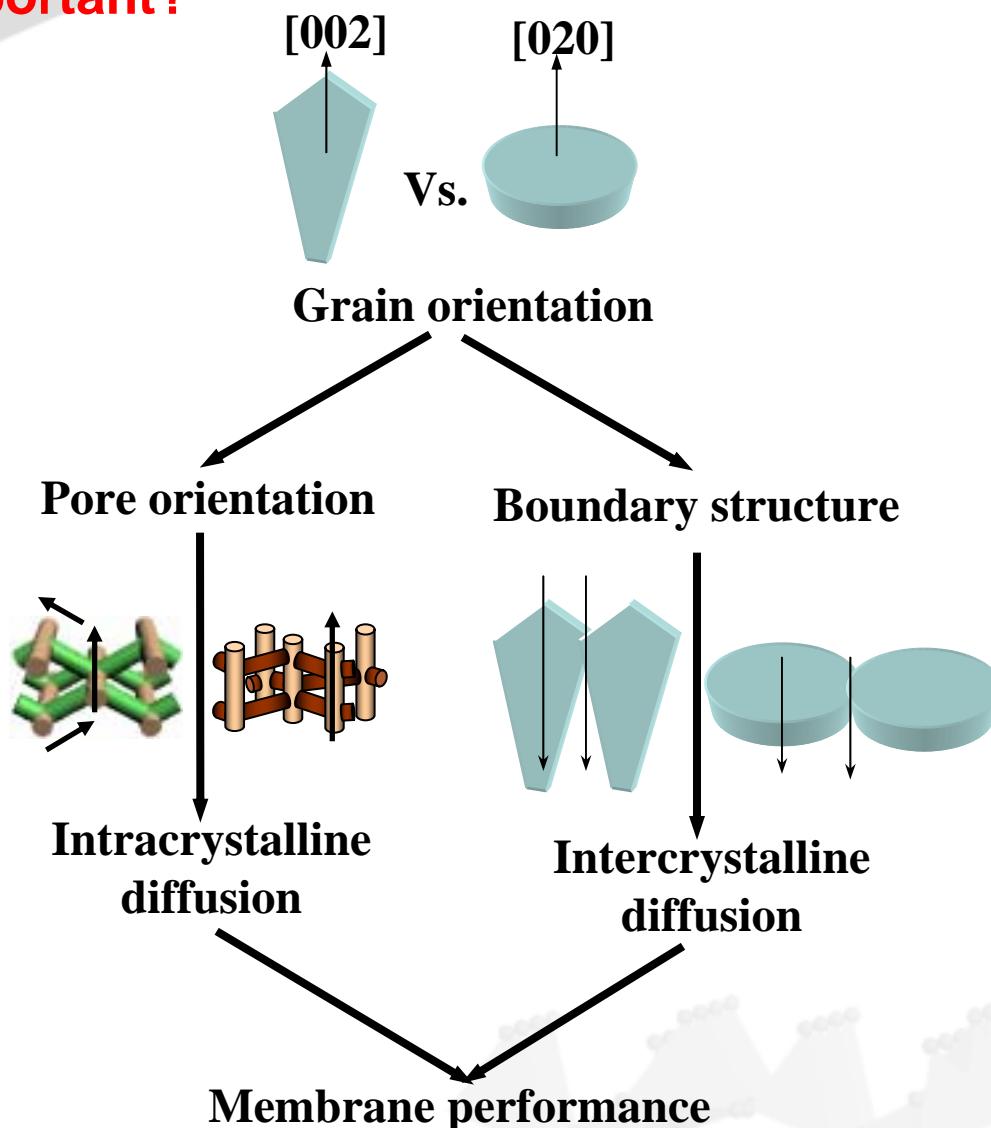
Randomly Oriented Seeds

substrate

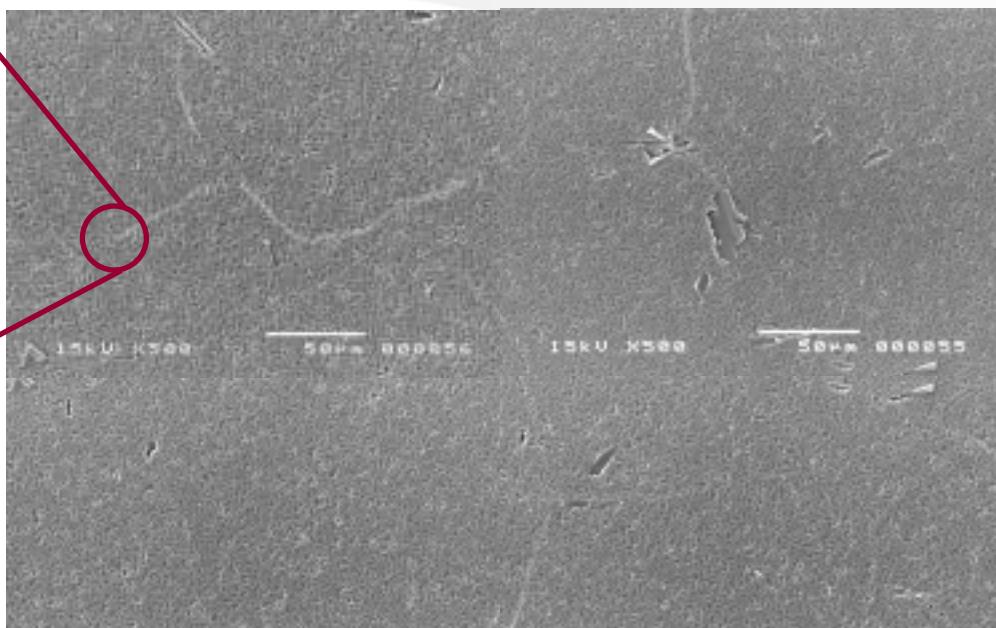
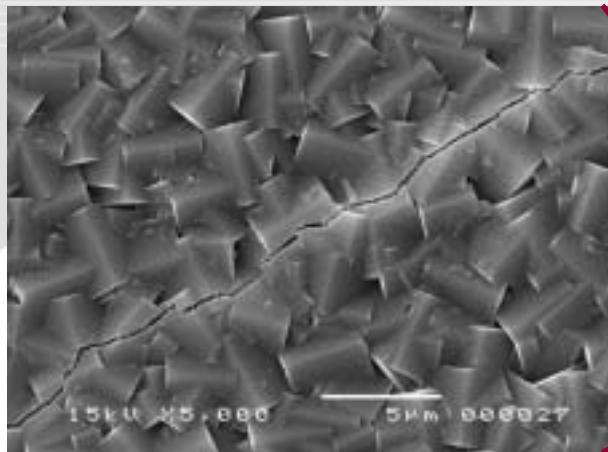


Chemistry of Materials 10, 2497-2504 (1998)

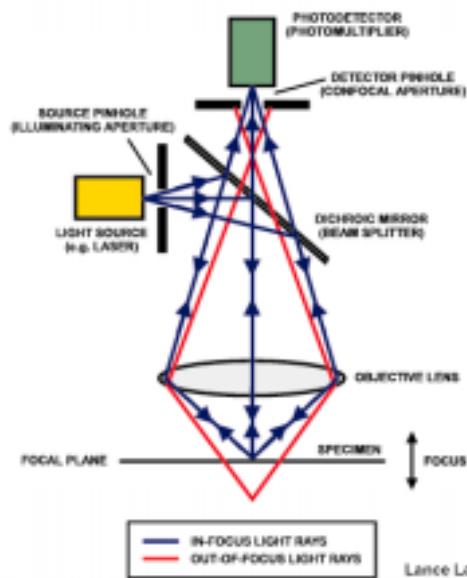
Why Membrane Orientation is Important?



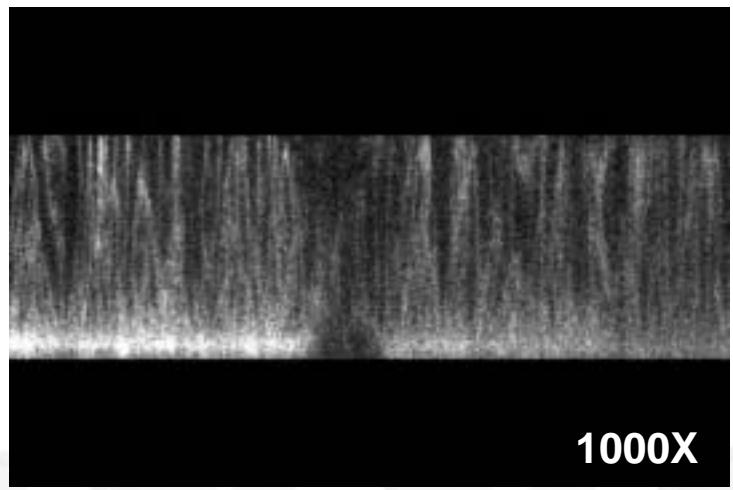
- Pore Orientation
- Grain boundary structure
- Crack-resistance upon calcination



SIMPLIFIED OPTICS OF A LSCM



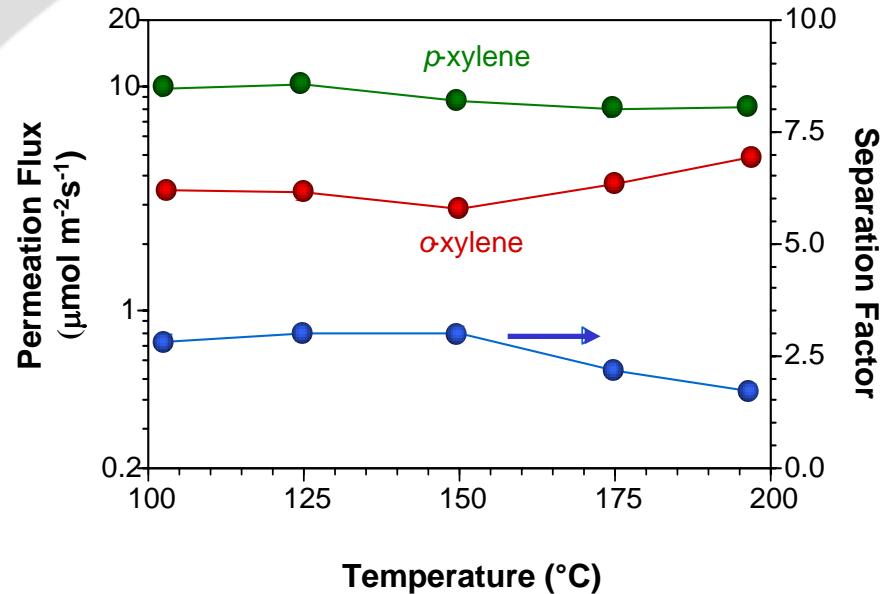
Fluorescent Dye of
Size larger than the
zeolite pore



Journal of Membrane Science 182:(1-2), 103-109 (2001)

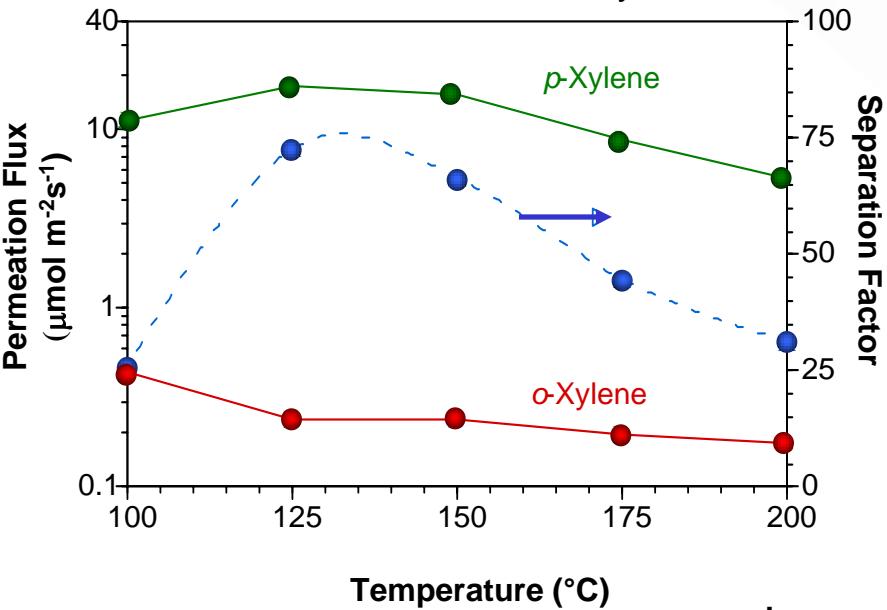
Membranes with c-out-of-plane orientation

Grain Boundaries Visible by FCOM

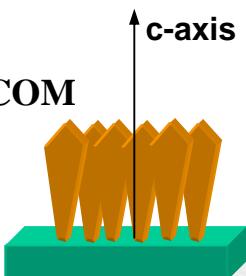


Membranes with $<\!h0h\!>$ -out-of-plane orientation

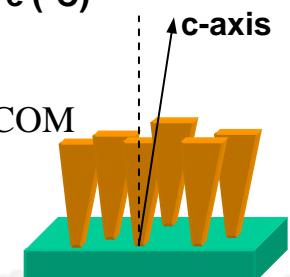
NO Grain Boundaries Visible by FCOM



Grain Boundaries Visible by FCOM
Low Density of Cracks

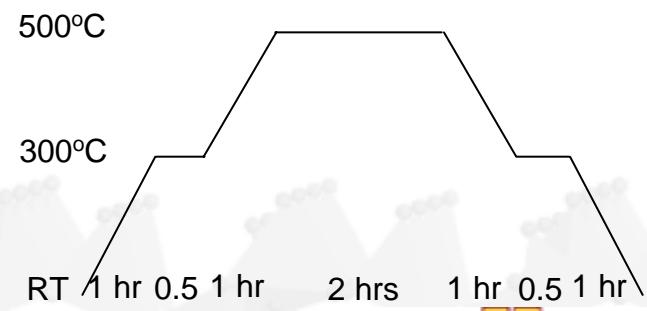
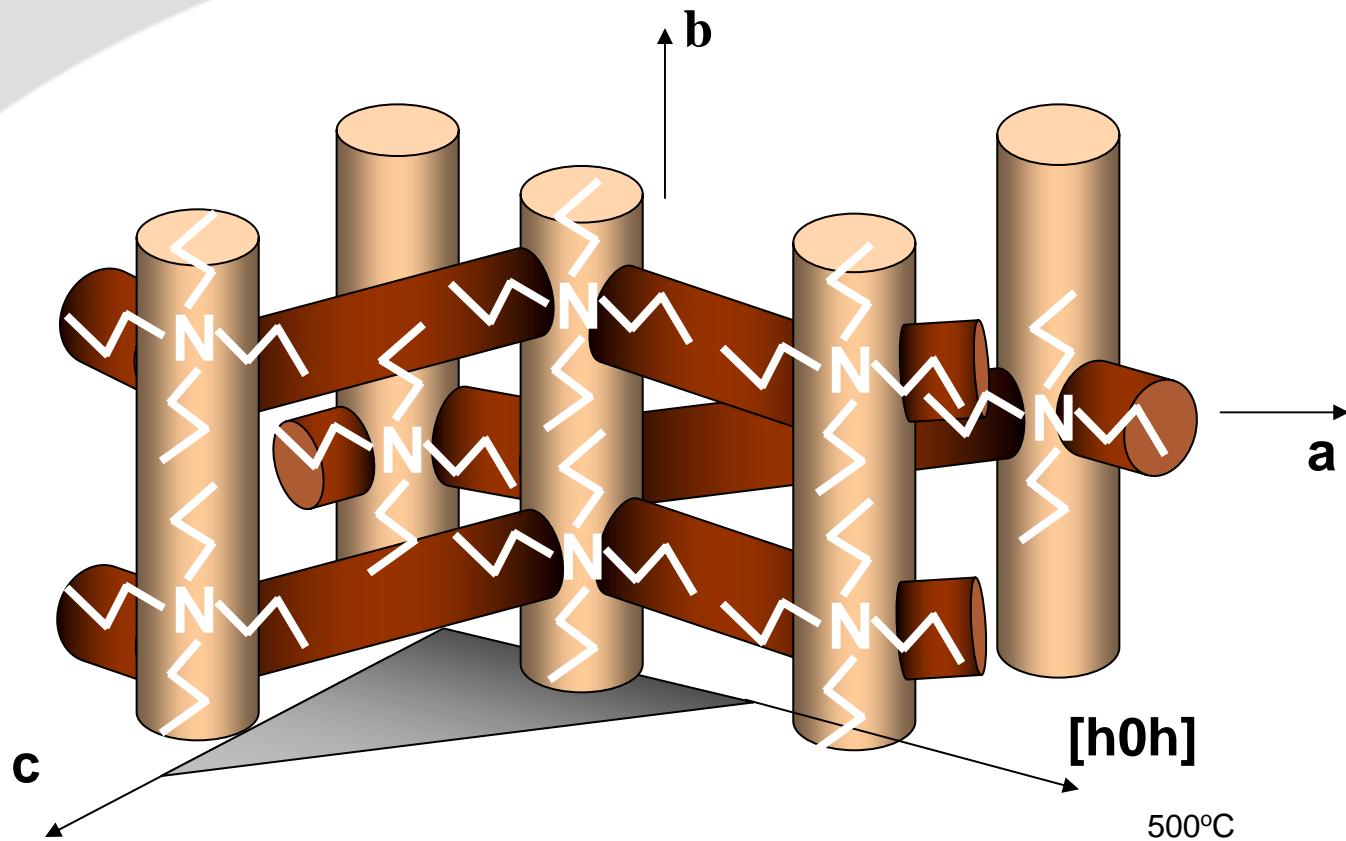


NO Grain Boundaries Visible by FCOM
High Density of Cracks
High Selectivity after crack reparation

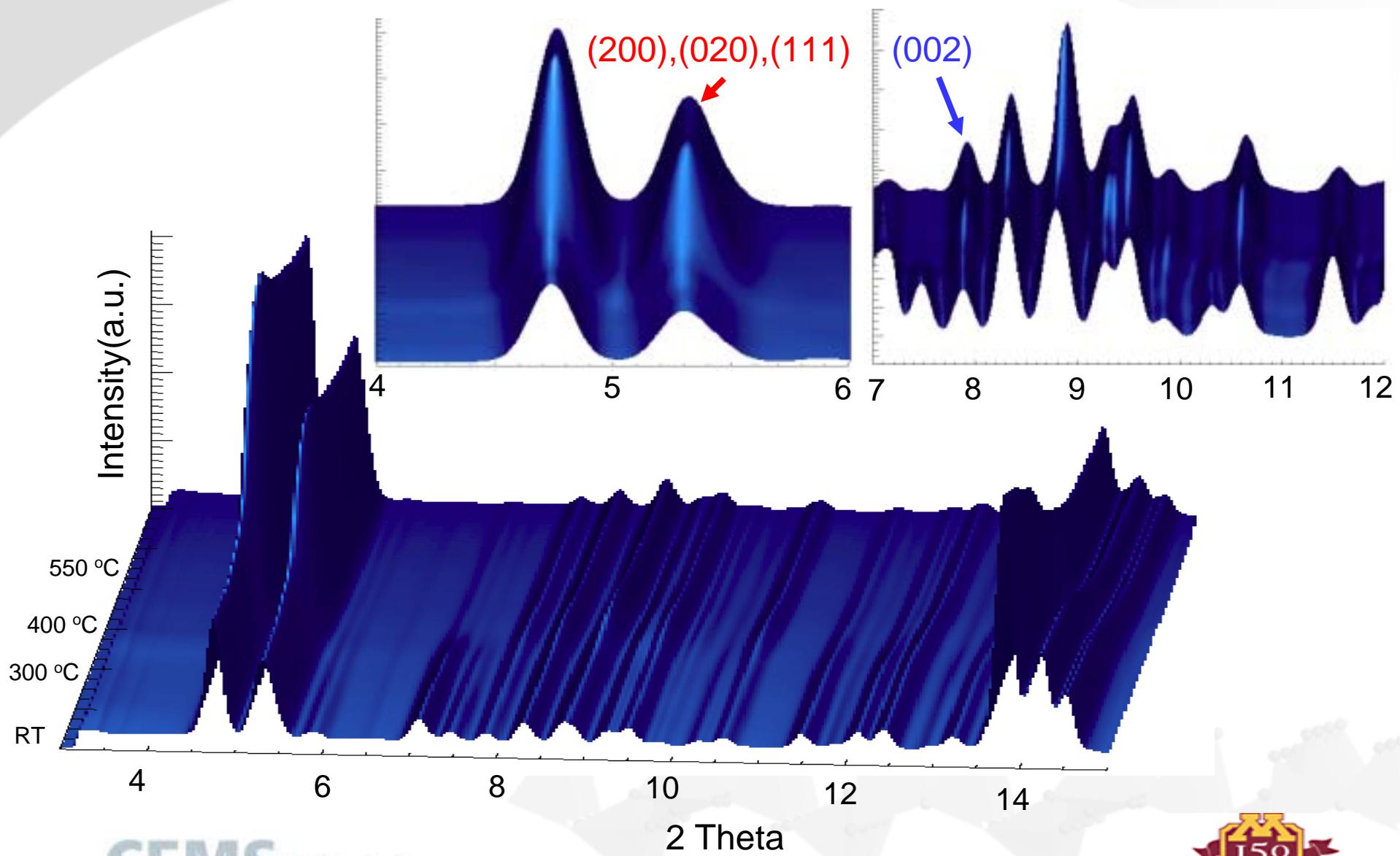


- Industrial and Engineering Chemistry Research **40**(2), 544-552 (2001)
- Journal of Physical Chemistry B. **104**(38), 8982-8988 (2000)
- Microporous and Mesoporous Materials **38**, 61-73 (2000)
- Chemical Engineering Science **54**, 3521-3531 (1999)
- Chemistry of Materials **11**, 875-878 (1999)

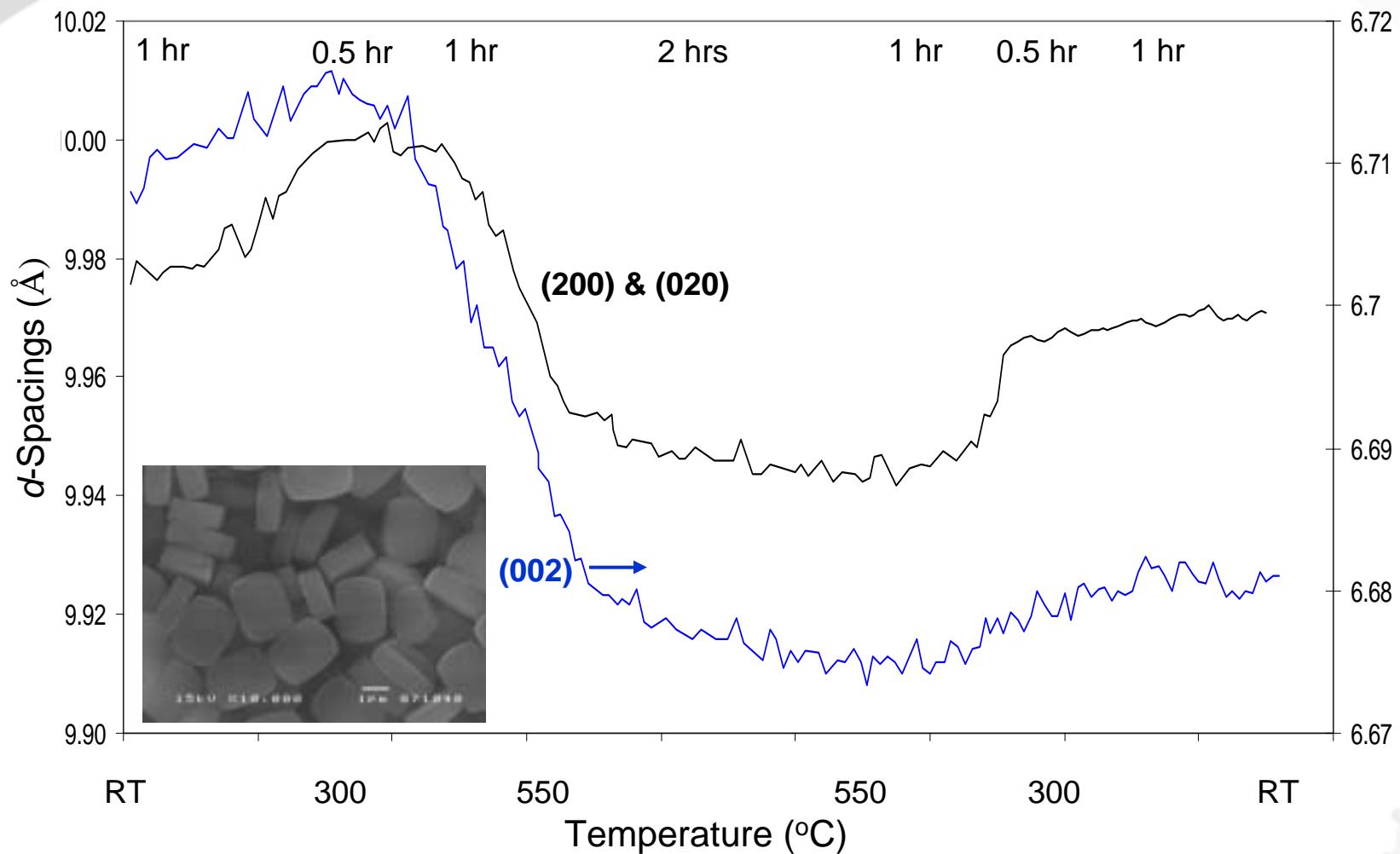
MFI Zeolite Upon Calcination of TPA



XRD Patterns of TPA MFI Powder During Calcination (with Hanson, BNL)

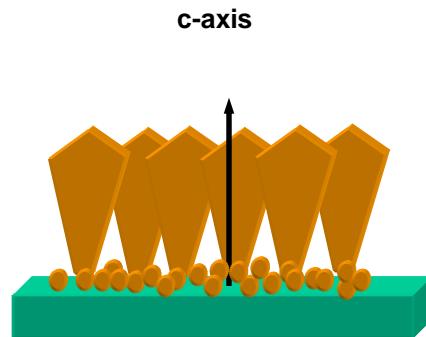


Resolution of d-Spacings of TPA MFI Powder Upon Calcination



Compared to Alumina

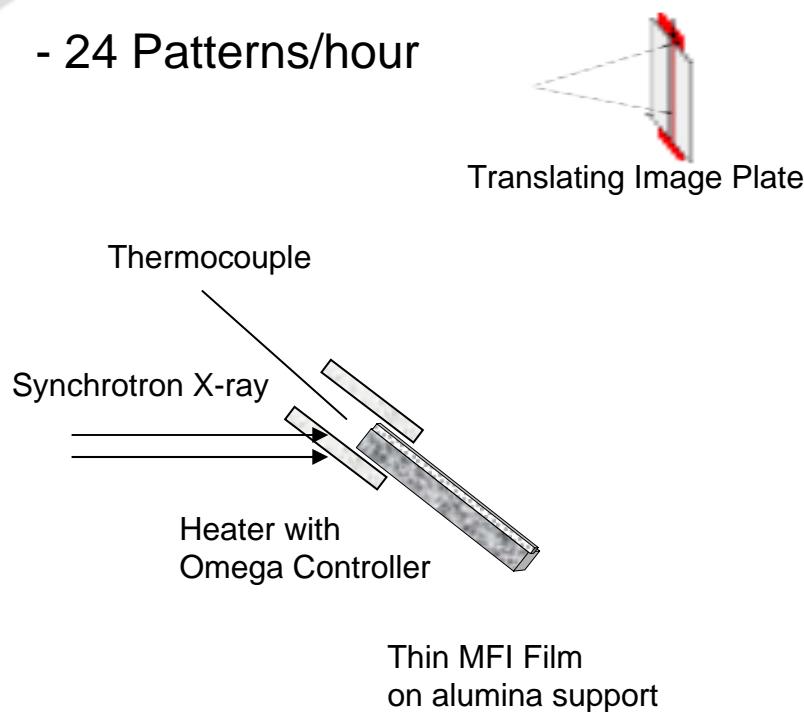
What will happen to MFI crystals grown on alumina support ???



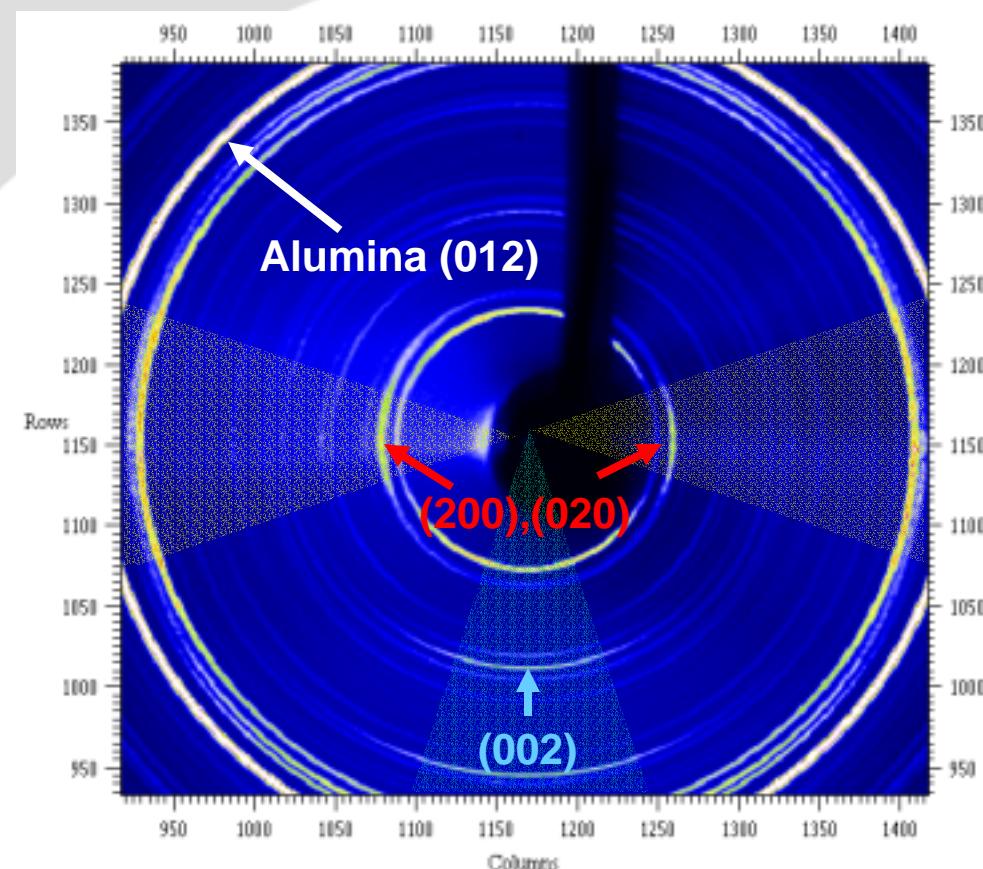
Experimental Setup for Membrane Samples at X7B BNL

- $\lambda = 0.92 \text{ \AA}$

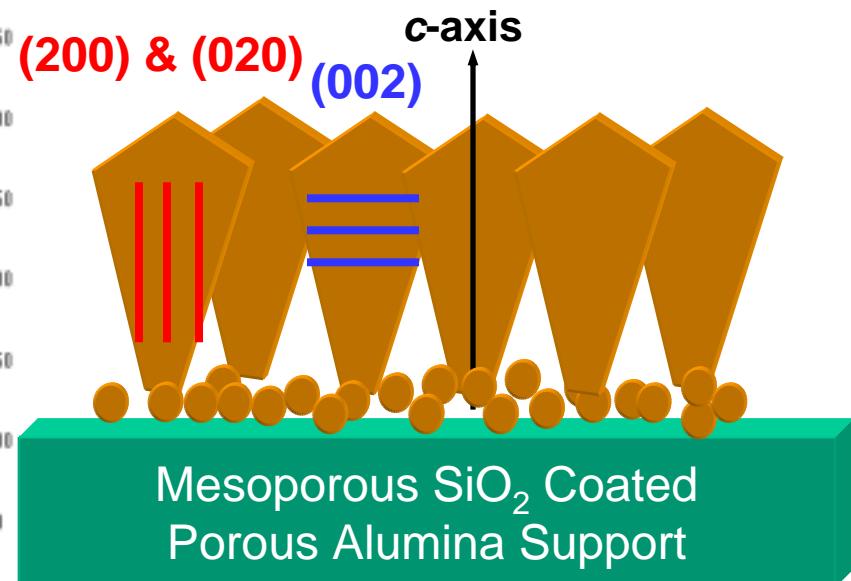
- 24 Patterns/hour



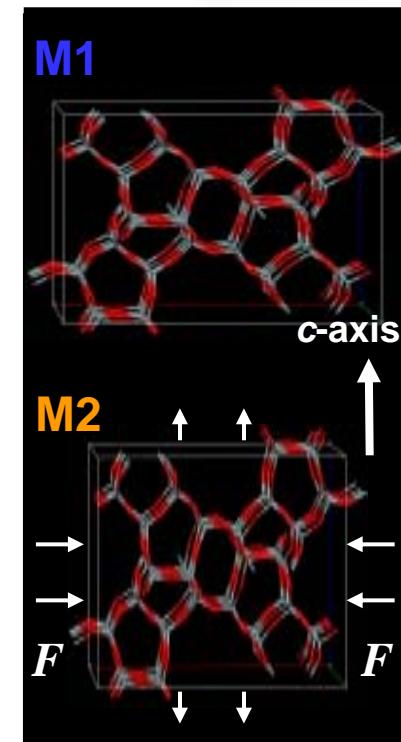
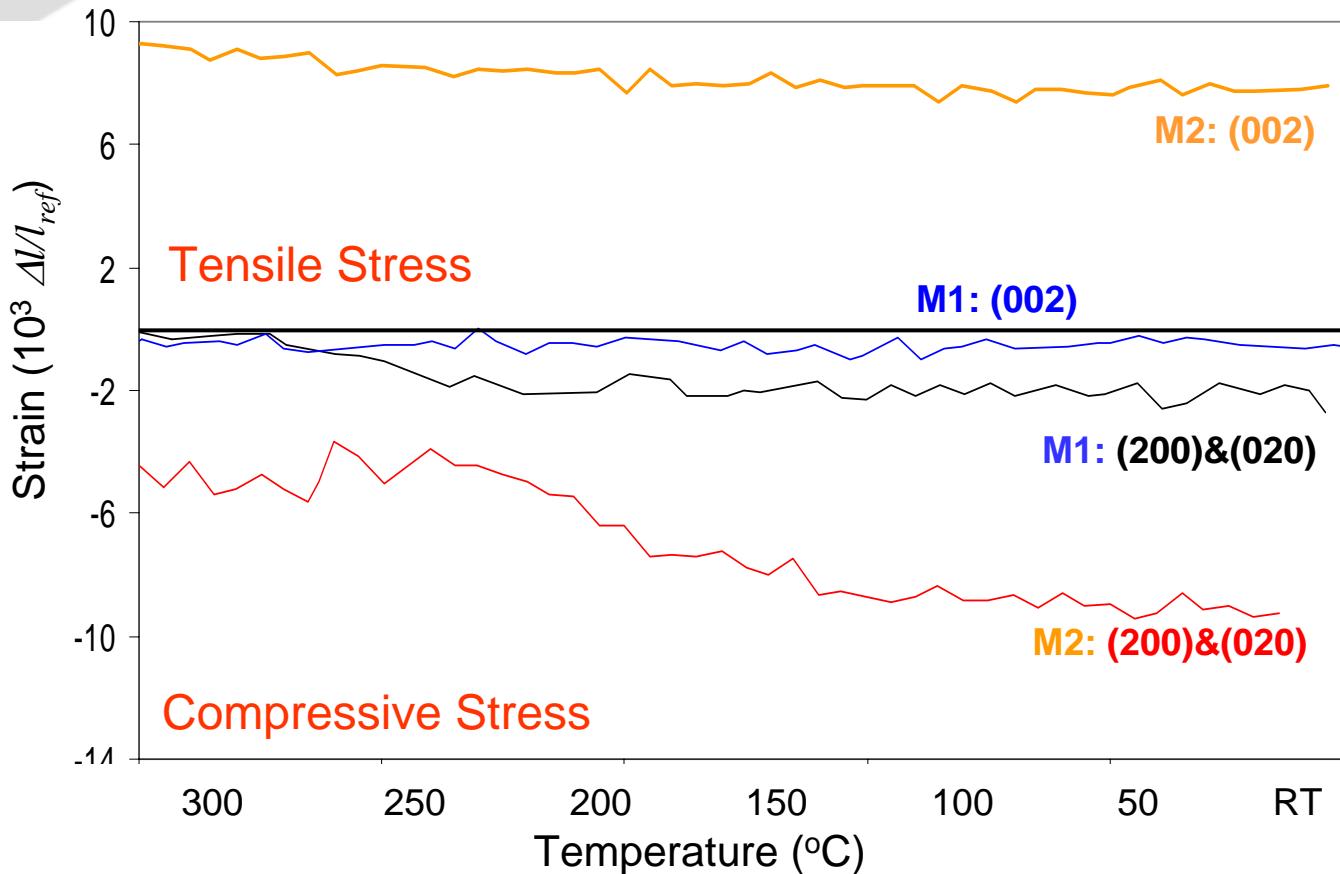
2D Diffraction Pattern from Oriented MFI Membrane (M1)



M1: c-oriented membrane

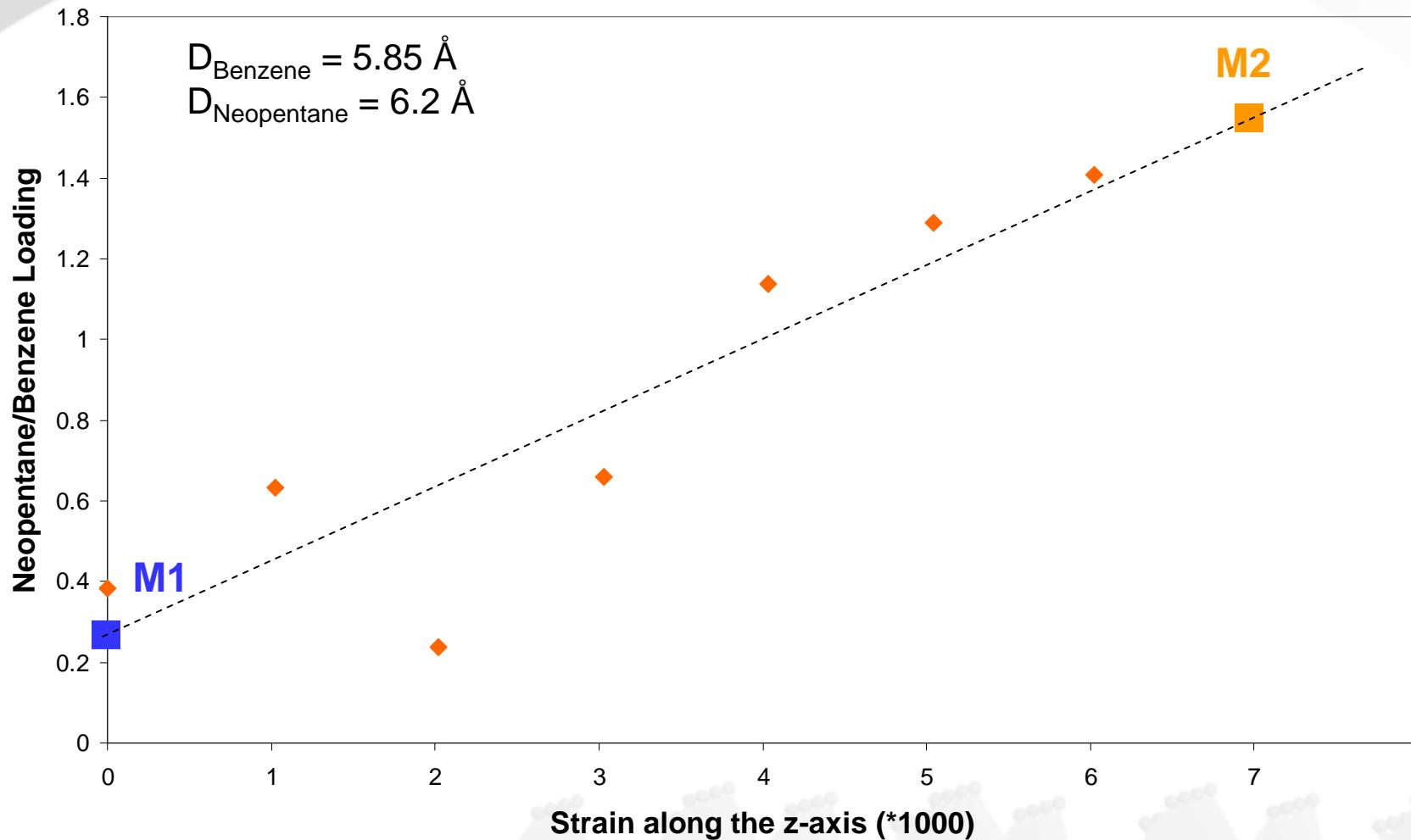


Strain of MFI Membranes of Different Microstrutures (M1 & M2)



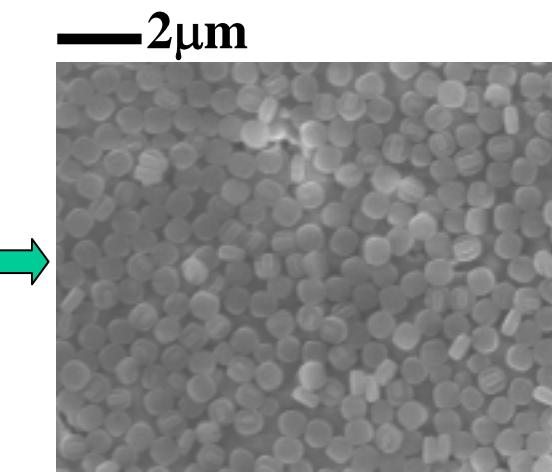
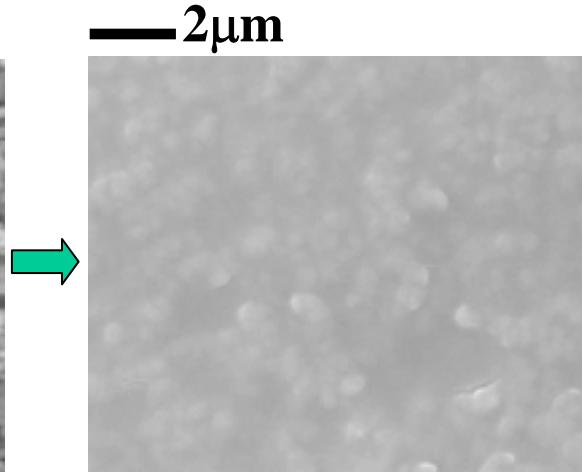
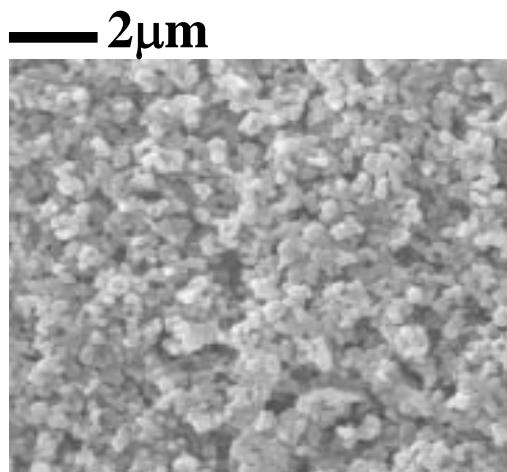
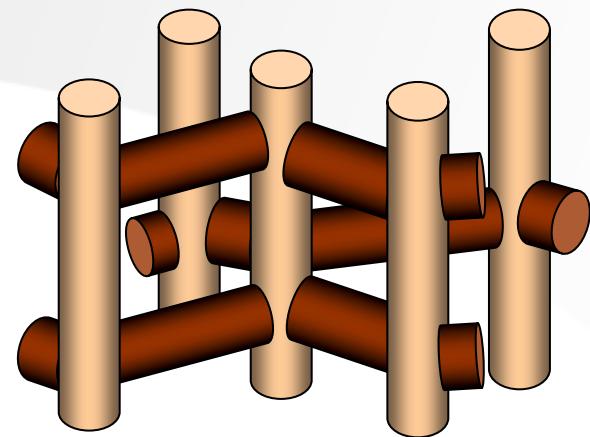
Thermal Strain ($\Delta l/l_{ref}$) = $(l(T) - l_{ref}(T))/l_{ref}(T)$, where $l_{ref}(T)$: d-spacing of MFI powder sample at each T.

Stress-Induced Tunable Molecular Sieves ?



J.N. Grima, et al. *Adv. Mater.* 2000

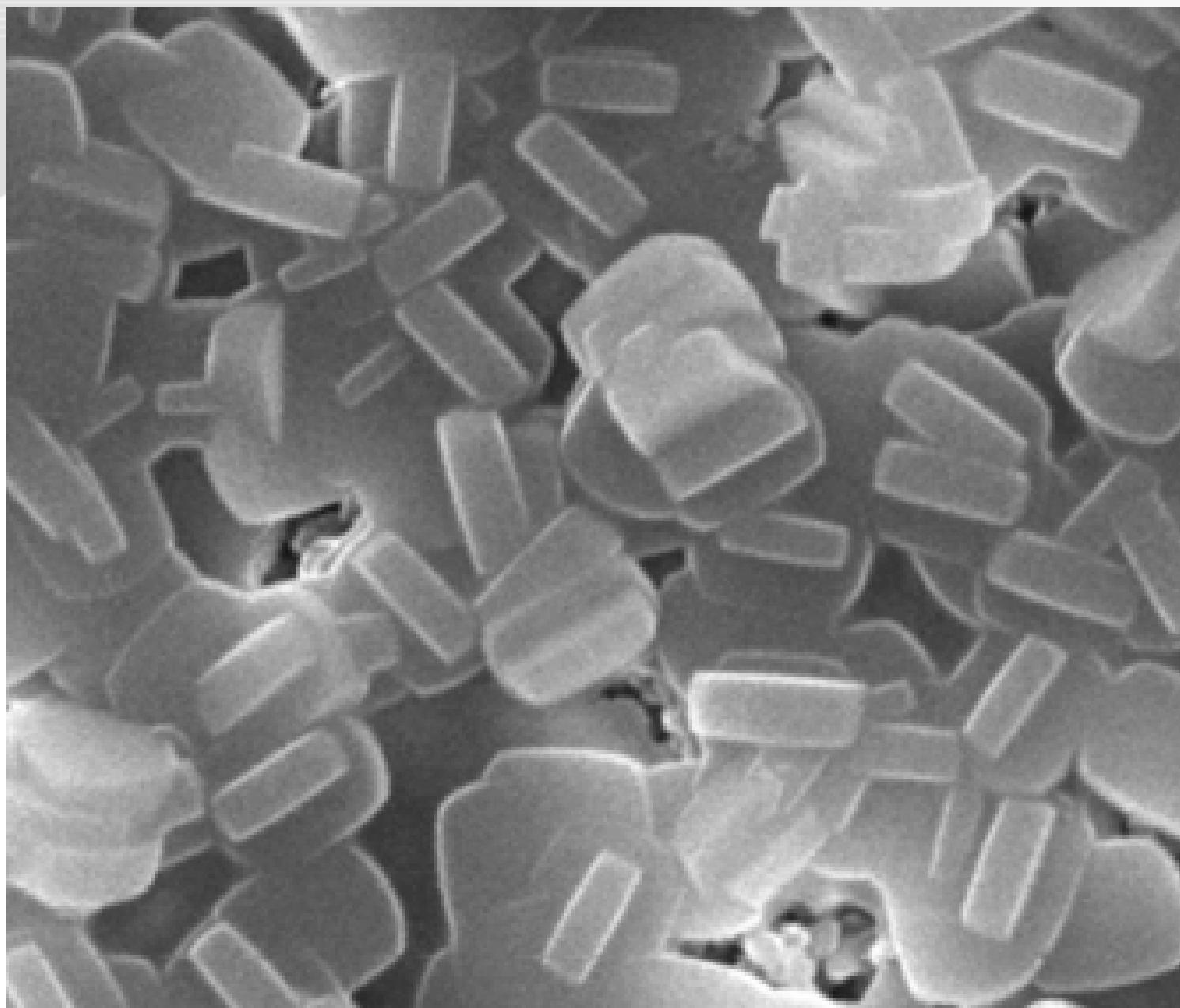
Preparation of b-oriented Seed Monolayers

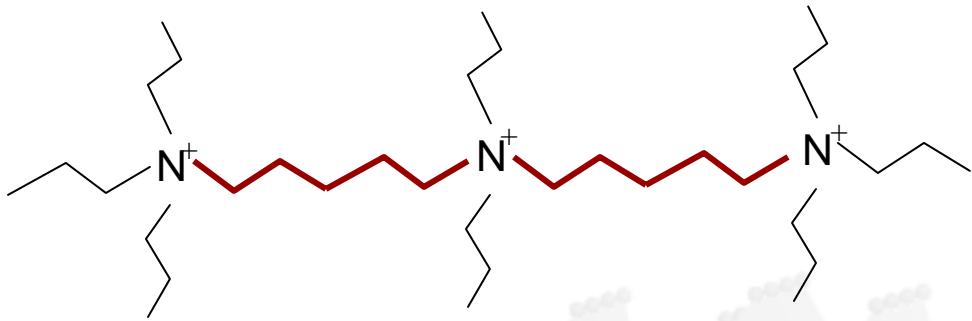
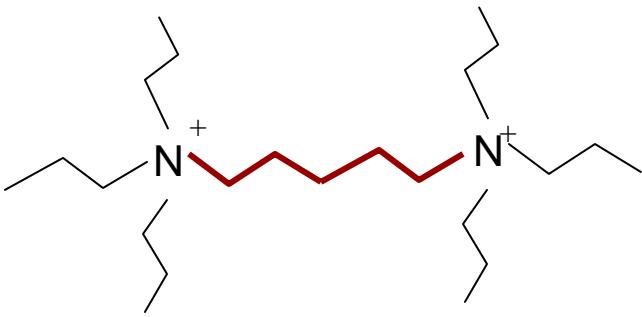
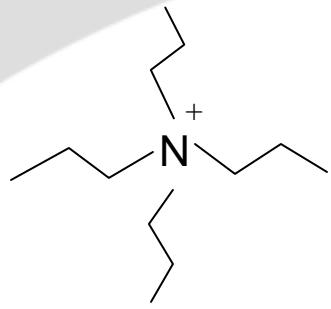


Lu, Y., et al., *Nature*,
389, 364 (1997)
(Brinker C. J.)

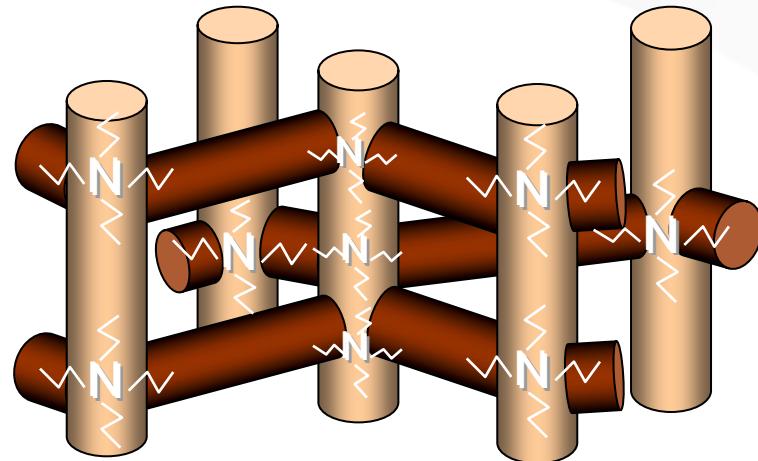
Ha, K., et al., *Adv. Mater.*,
12, 1114, (2000)
(Yoon K. B.)

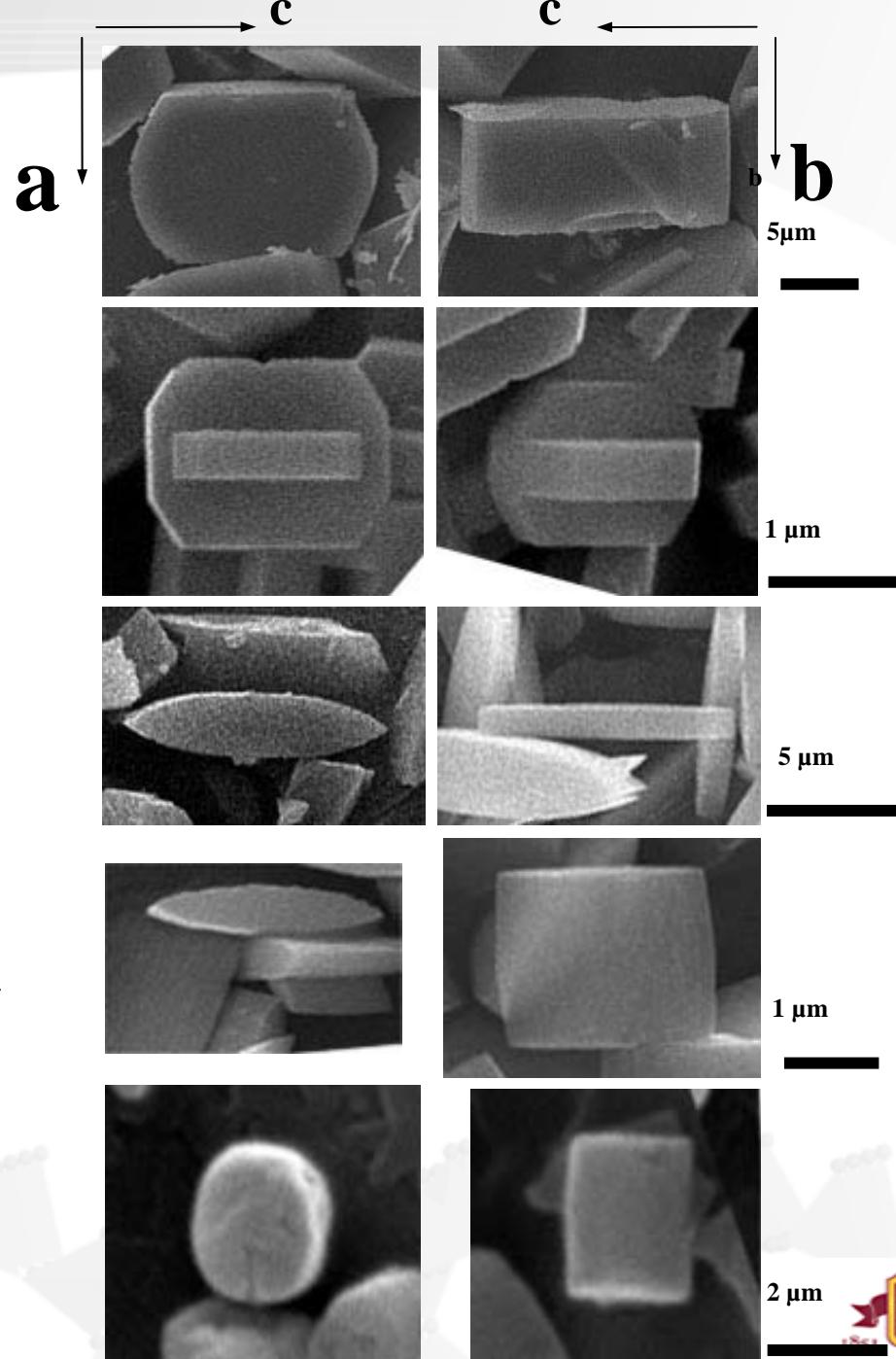
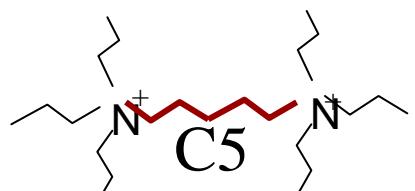
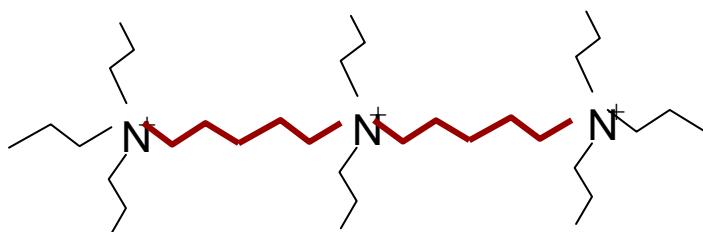
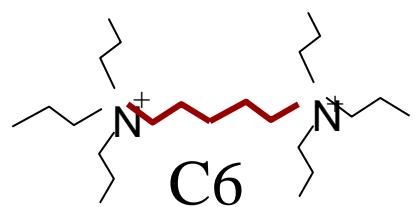
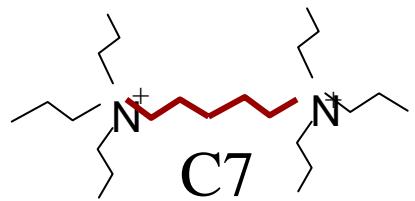
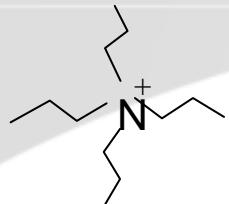
2 μ m

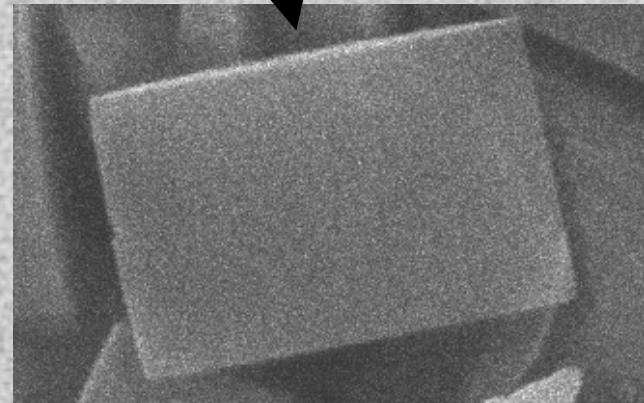


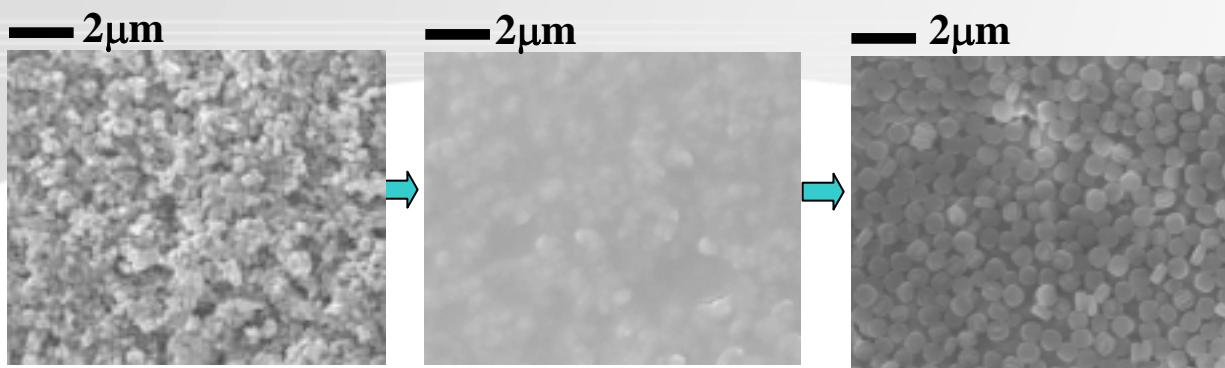


C5-C7



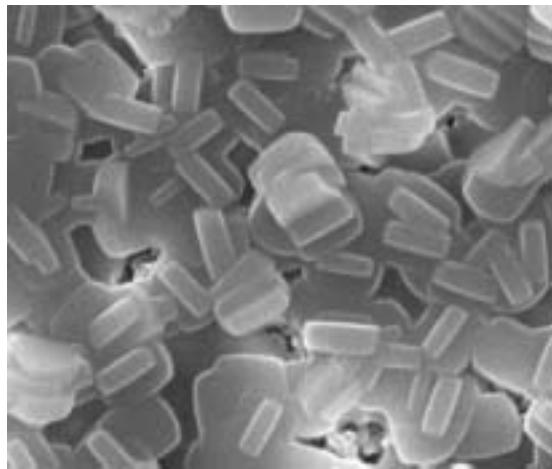
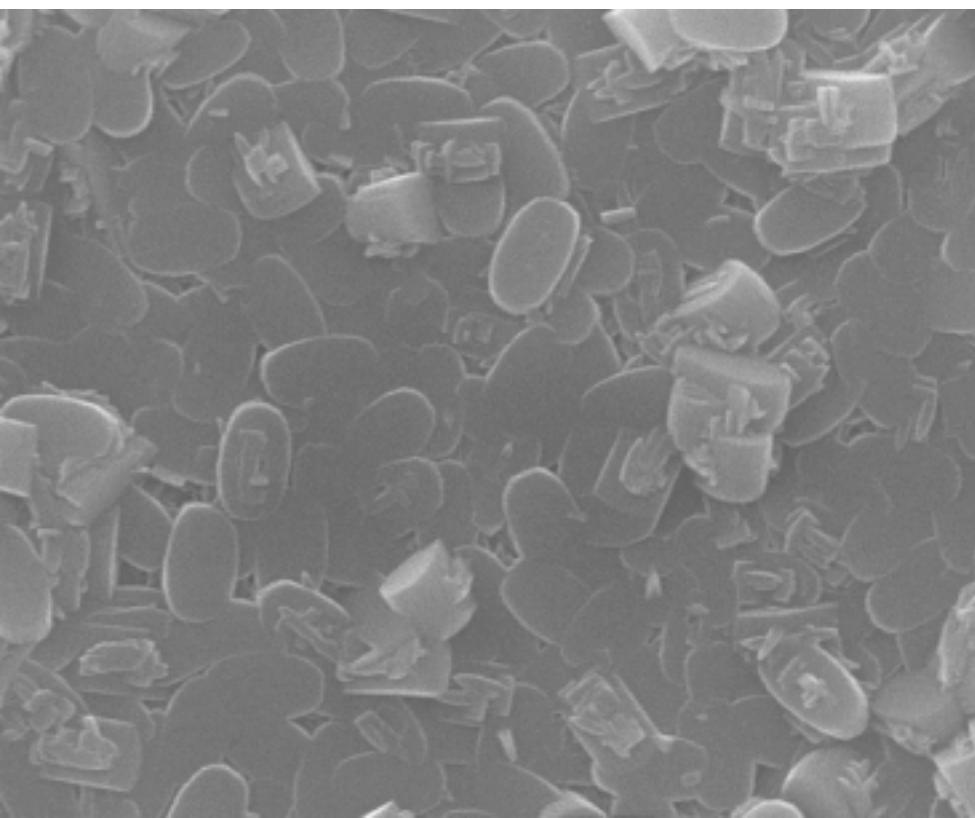


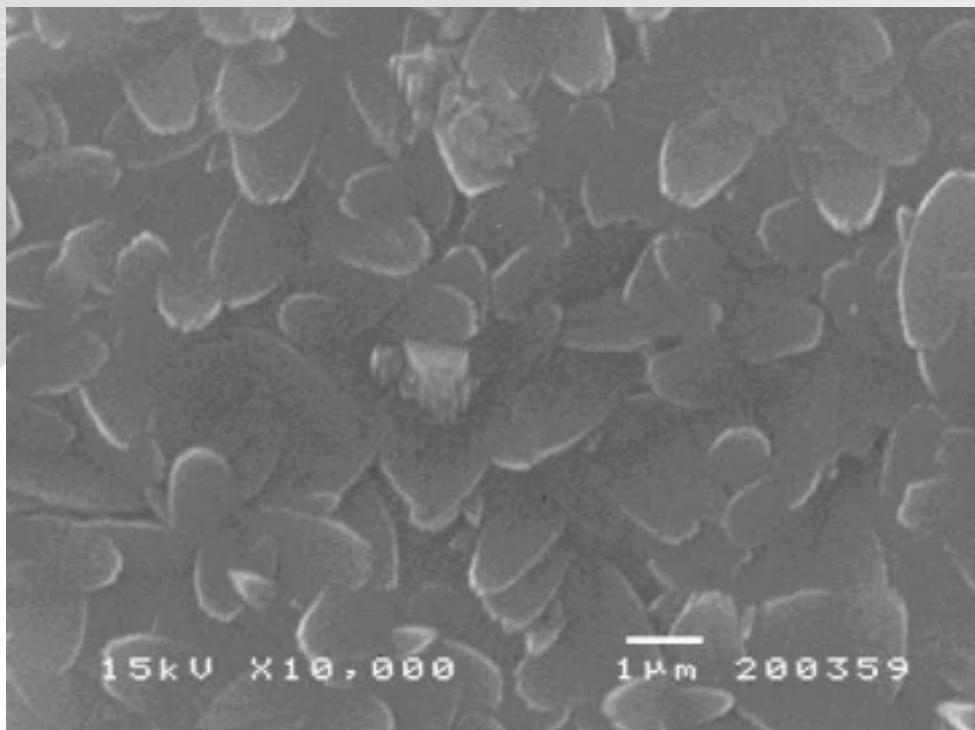




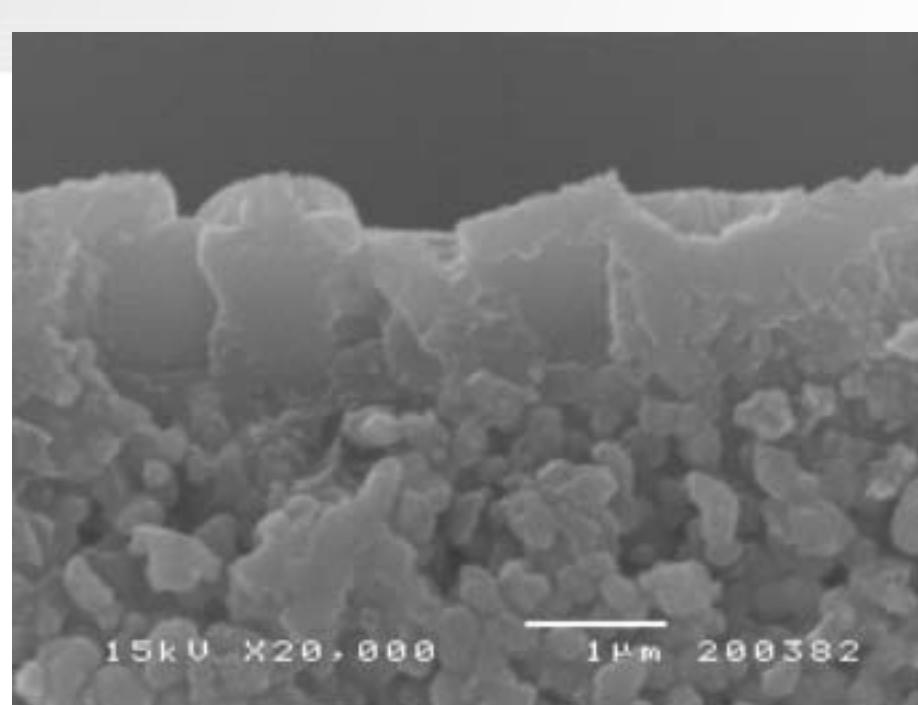
Trimer TPA
2μm

TPA
2μm

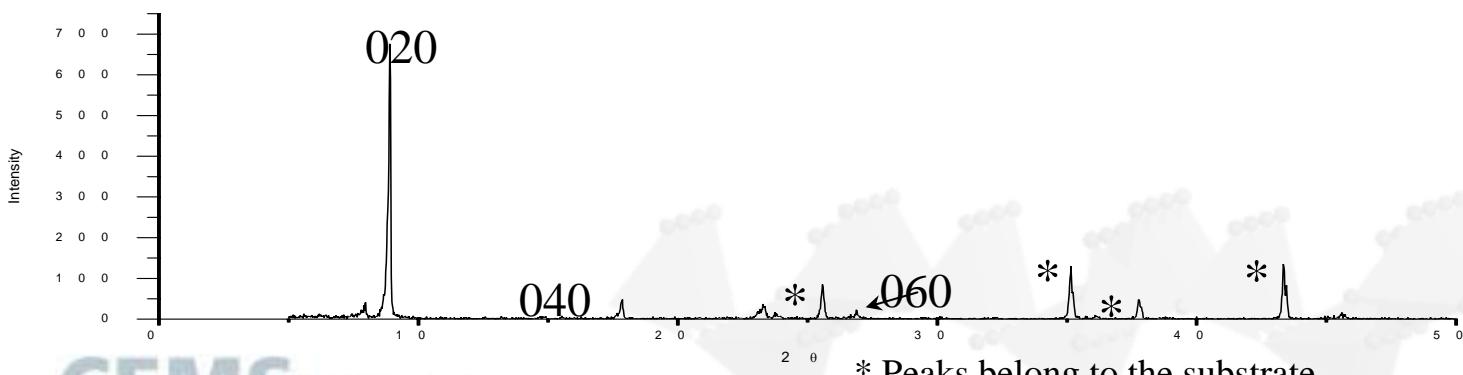




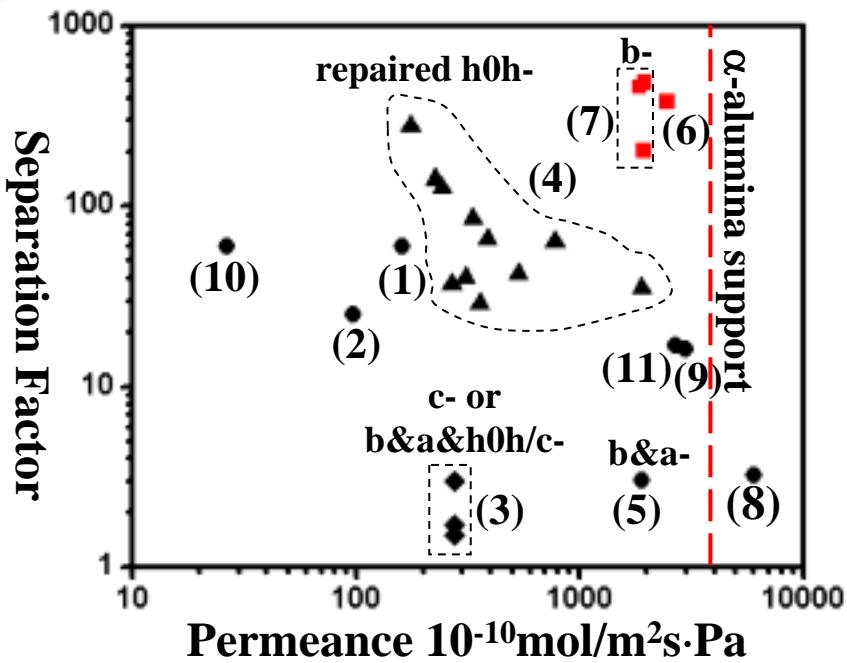
Top View



Cross Section



Comparison with Reported Results



Explanation of symbols in the Figure

No.	Source	Orientation	Thickness (μm)	Temp (°C)
1	Keizer K. et al., 1998	random	3	125
2	Keizer K. et al., 1998	random	3	200
3	Xomeritakis G. et al., 1999	c	30	150
4	Xomeritakis G. et al., 2001	h0h	1	130
5	Present work	b&a	1	180
6	Present work	b	1	150
7	Present work	b	1	200
8	Hedlund J. et al., 2002	random	0.5	100
9	Hedlund J. et al., 2002	random	0.5	390
10	Gump C.J. et al., 2001	random	---	150
11	Hedlund J. et al., 2003	random	0.5	400



Microstructure Characterization

Permeation Properties Mechanical Properties

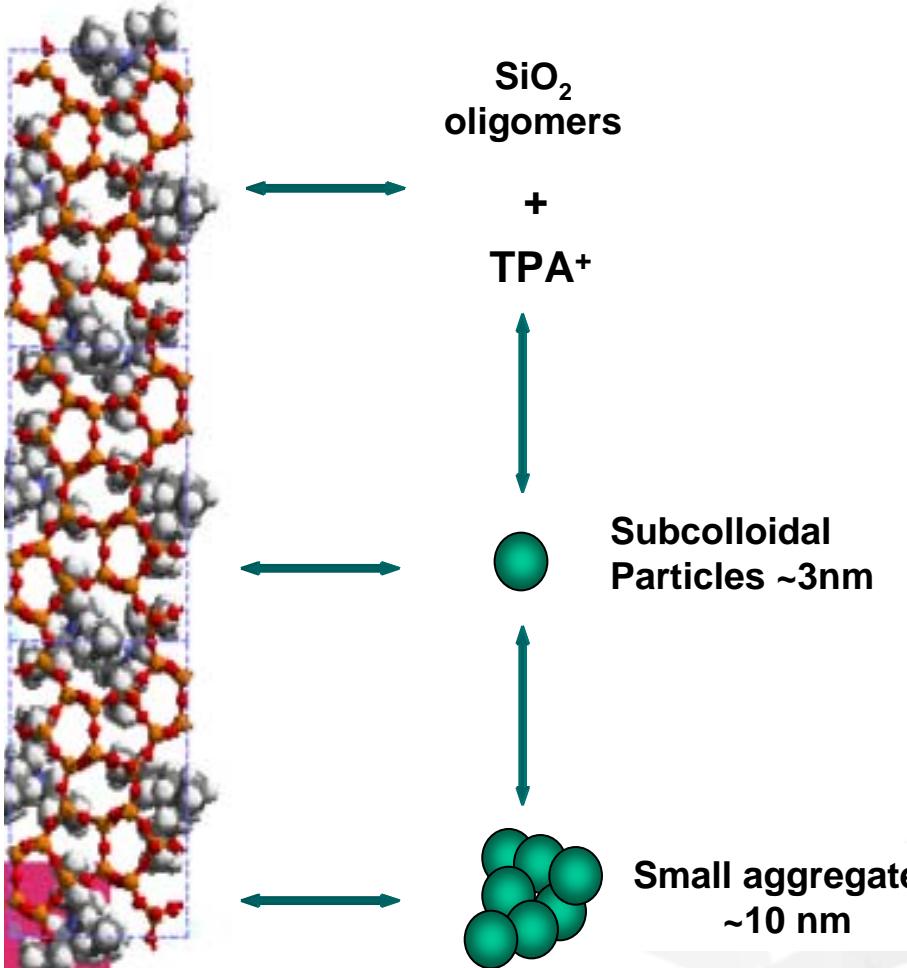
Microstructure Control ?

Properties Prediction?



Zeolite Growth “Mechanism”

Silicalite-1 surface

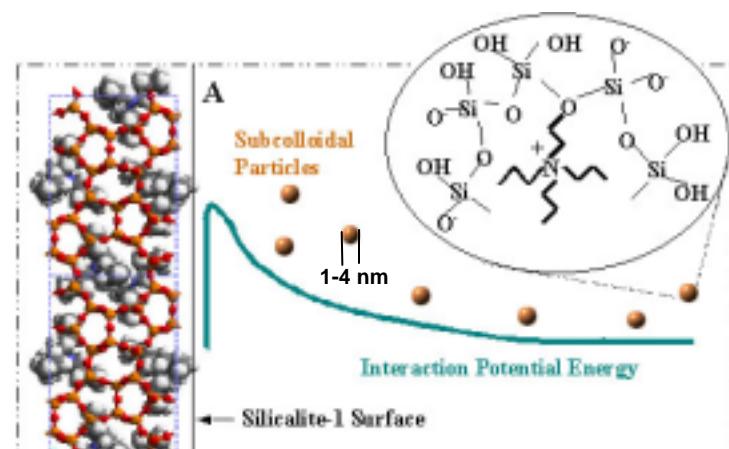


Many experimental studies:

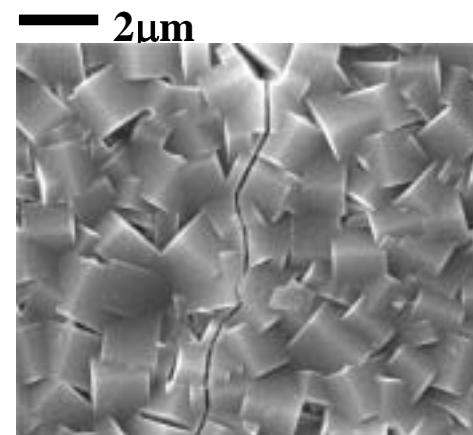
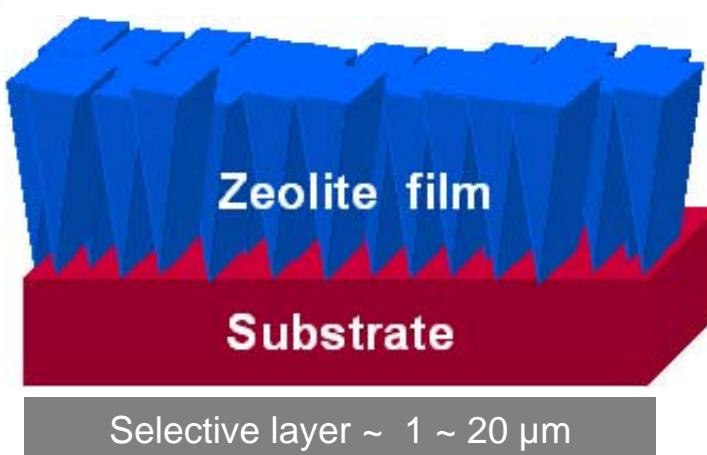
- Ravishankar R. et al. *J. Phys. Chem.* 103, 4960 (1999)
P.P.de Moor et al. *Chemistry-A European Journal* 5, 2083 (1999)
Watson et al. *J. Phys Chem B* 101, 10094 (1997)
Schoeman et al. *Zeolites* 14, 568 (1994)
Twomey T.A.M. et al. *Zeolites* 14, 162 (1994)

Very few modeling studies:

- Nikolakis et al. *Chem Mater.* 12, 845-853 (2000)



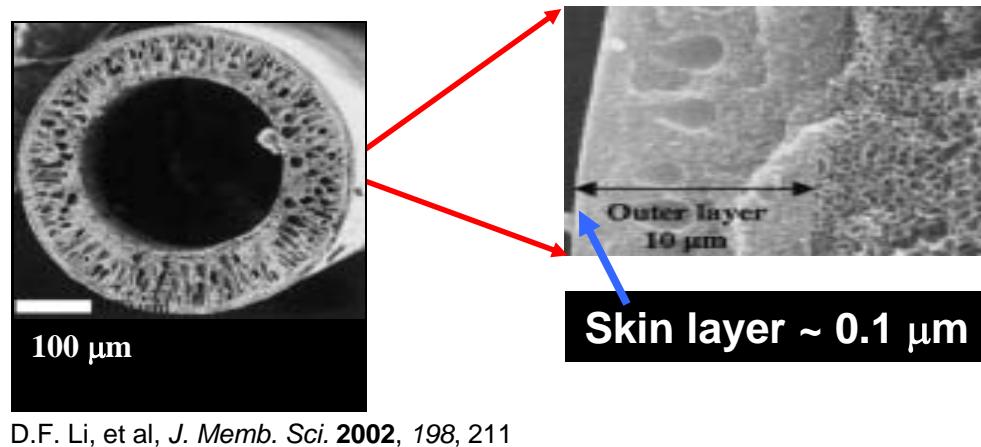
Zeolite Membrane: Limitations



- Fragile**
- Expensive**
- Scale up still to be demonstrated**

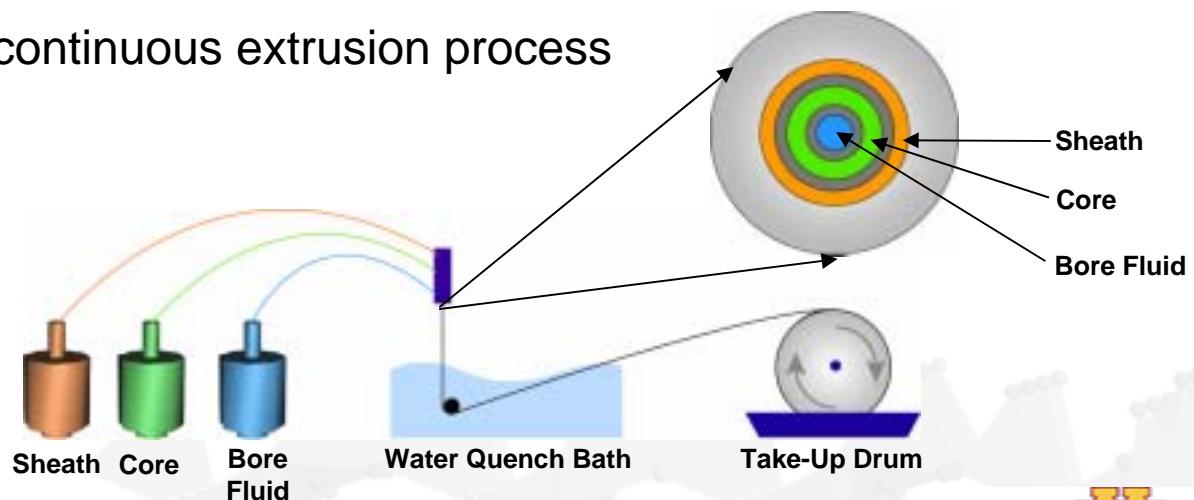
Polymer Membrane

- **Processability** : ability to achieve thin selective skin layer in hollow fiber



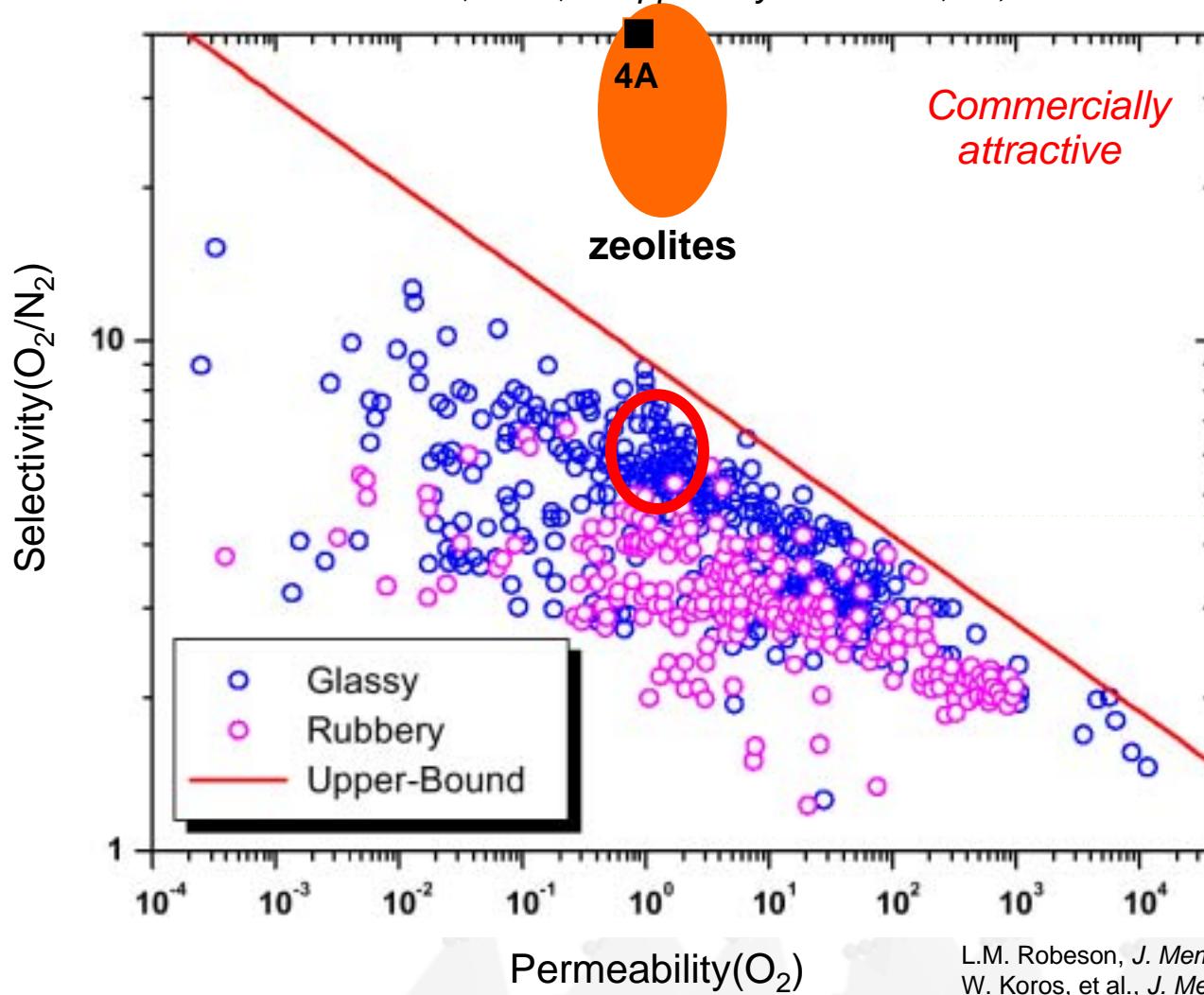
D.F. Li, et al, *J. Memb. Sci.* **2002**, 198, 211

- **Cost effective** : continuous extrusion process



Polymer Membrane: Limitations and

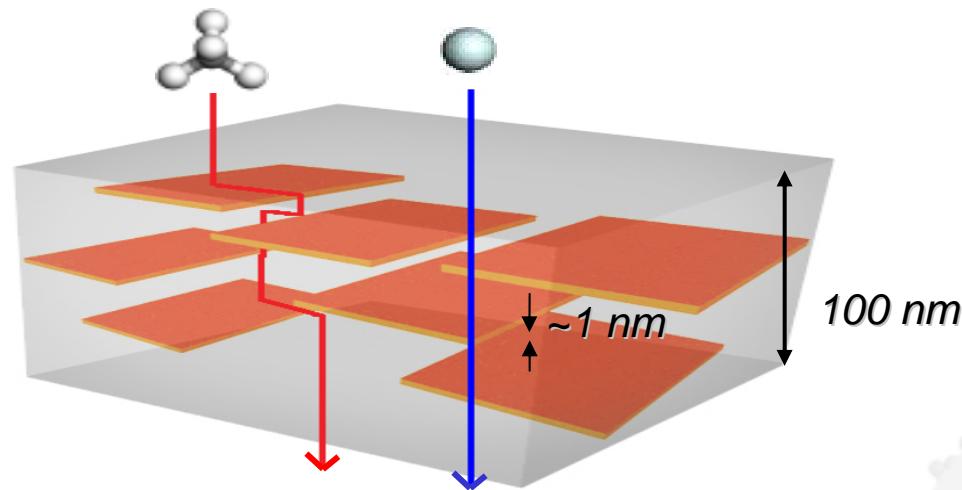
Mixed Matrix Membranes W. Koros, et al., *J. Appl. Poly. Sci.* 2002, 86, 881



L.M. Robeson, *J. Memb. Sci.* 1991, 62, 165
W. Koros, et al., *J. Memb. Sci.* 1997, 137, 145

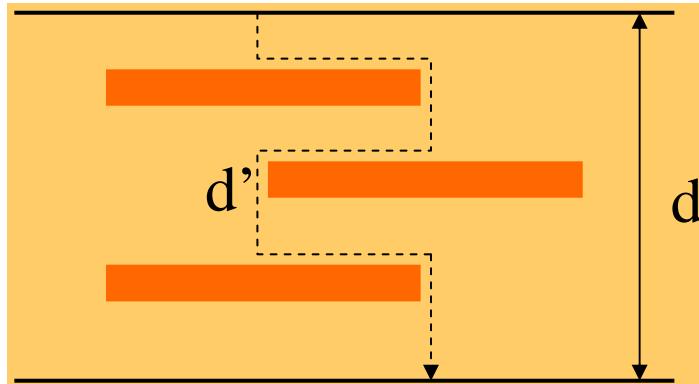
***To incorporate molecular sieves
without sacrificing good properties of polymer !!***

- Use selective molecular sieves much thinner than 100 nm*
- Add small amount of molecular sieves (< 10 %)*



Tsapatsis, Jeong and Nair, US patent USSN 60/391,988 (2002)

From Barrier to Selective Nanocomposite

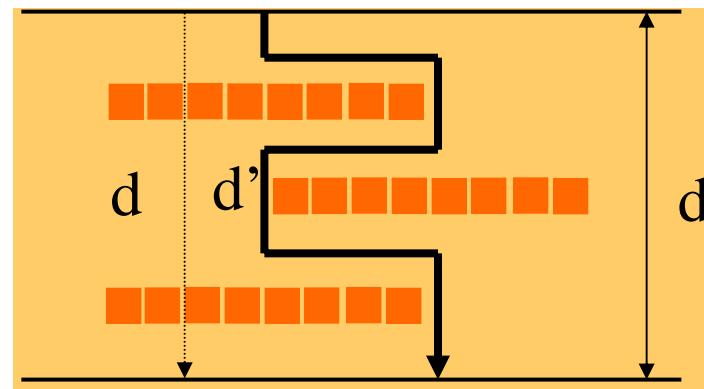


Impermeable Layers

$$\frac{J_{\text{Membrane}}}{J_{\text{Polymer}}} = \frac{1}{1 + \alpha^2 \phi^2 / (1 - \phi)}$$

$\delta = \frac{D_{\text{Polymer}}}{D_{\text{Layer}}}$, $\phi = \text{volume fraction}$, $\alpha = \text{aspect ratio}$

- R. Aris, *Arch. Rotin. Mech. Anal.* **1986**, 95, 83
R. M. Barrer, et al., *British J. Appl. Phys.* **1991**, 12, 691
E.L. Cussler, *J. Memb. Sci.* **1988**, 38, 161
E.L. Cussler, et al., *J. Memb. Sci.* **1996**, 119, 129
G.H. Fredrickson, *J. Chem. Phys.* **1999**, 110, 2181

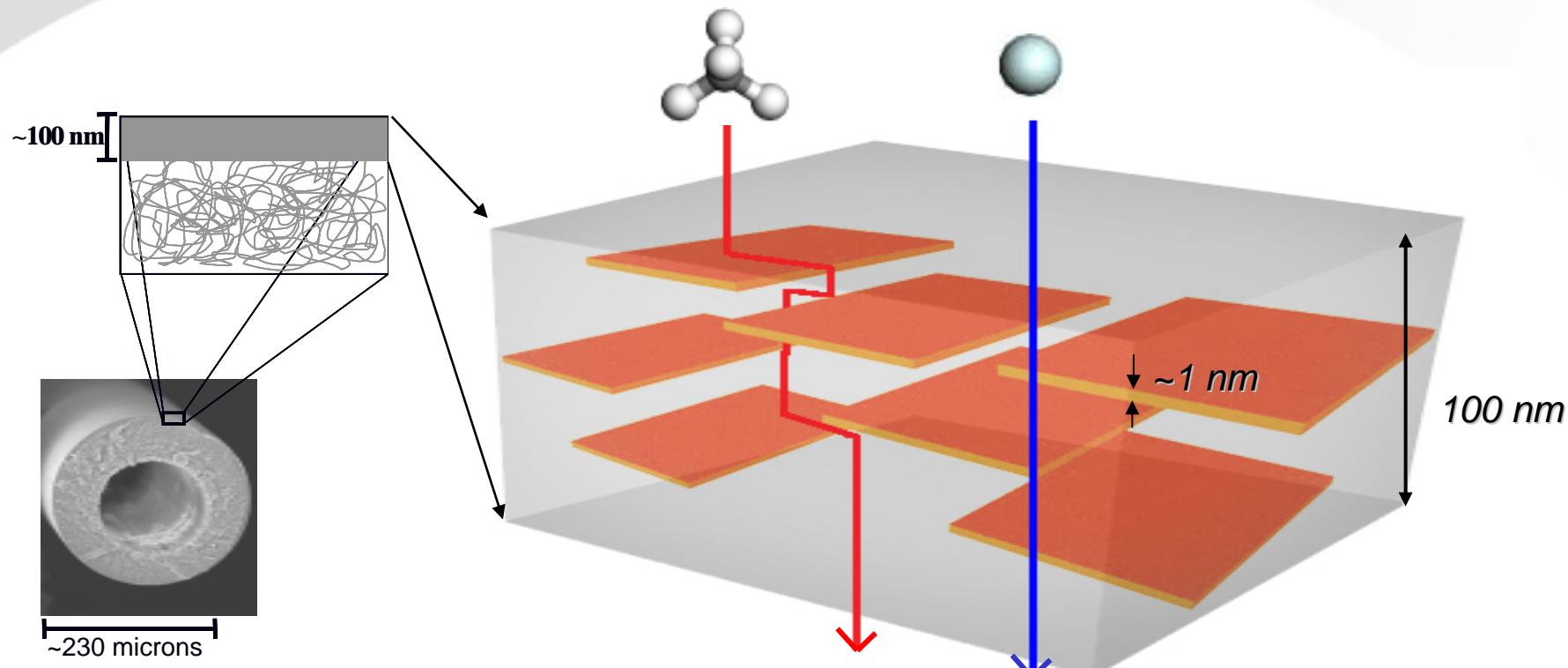


Selective Layers

$$\frac{J_{\text{Membrane}}}{J_{\text{Polymer}}} = \frac{1}{1 - \phi + \left[\frac{1}{\frac{1}{\delta \phi} + \frac{1 - \phi}{\alpha^2 \phi^2}} \right]}$$

- E.L. Cussler, *J. Memb. Sci.* **1990**, 56, 275

Selective Nanocomposite Membrane



POLYMER MATRIX

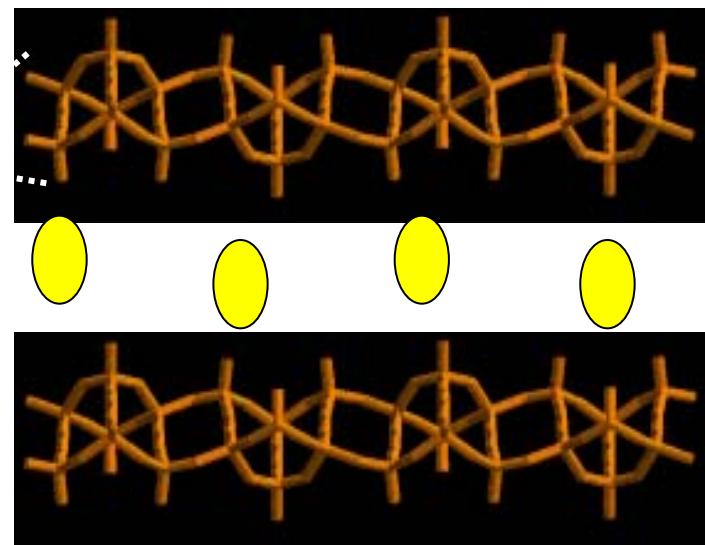
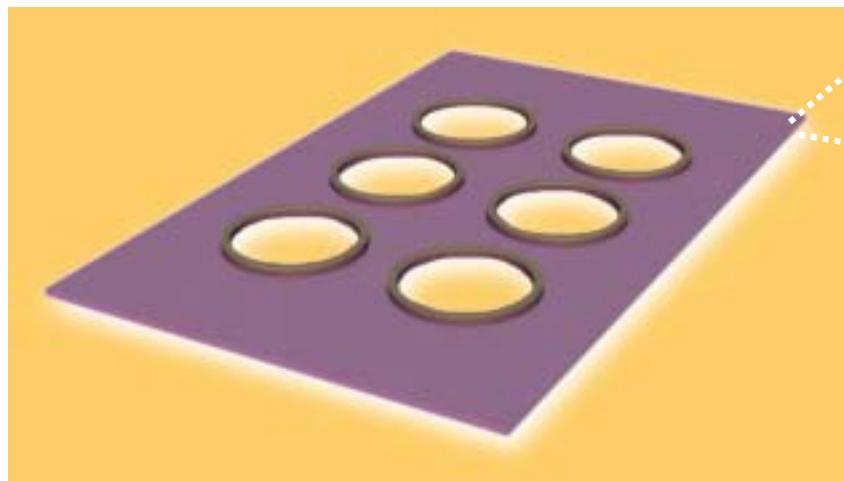
processability
solution-diffusion selectivity
mechanical strength

NANOPOROUS LAYERS

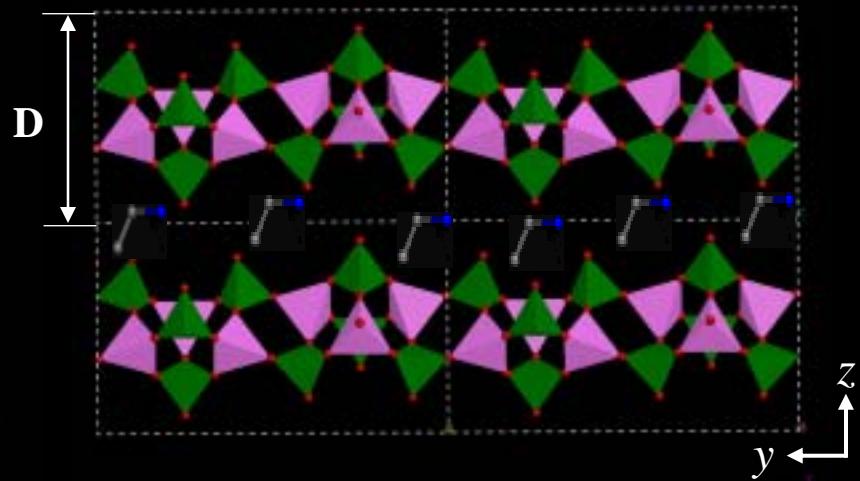
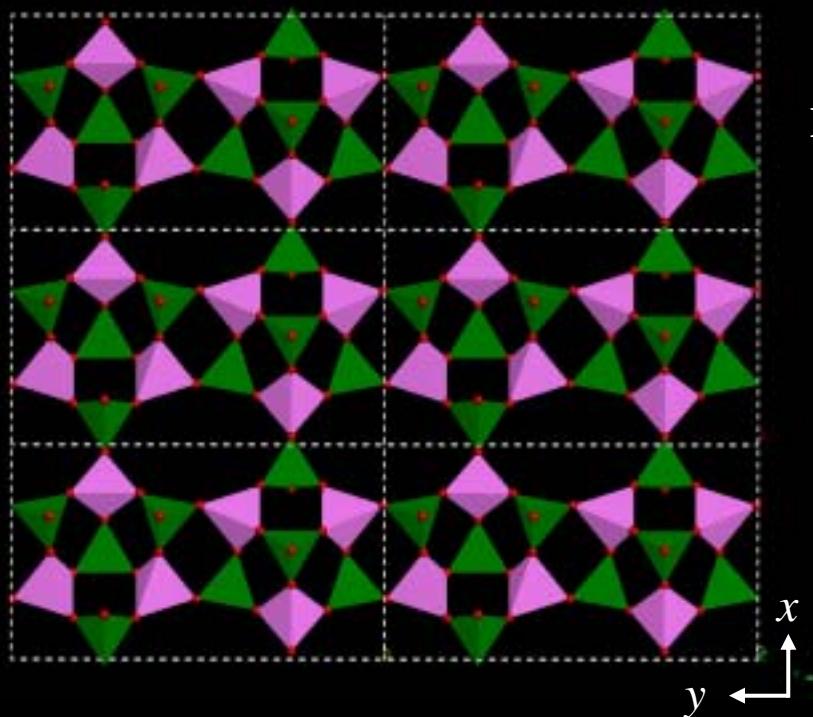
molecular sieving
adsorption selectivity
mechanical strength
thermal stability

Layered Material with Selective Layers

Layered Aluminophophates



Porous Layered Aluminum Phosphate (AlPO)

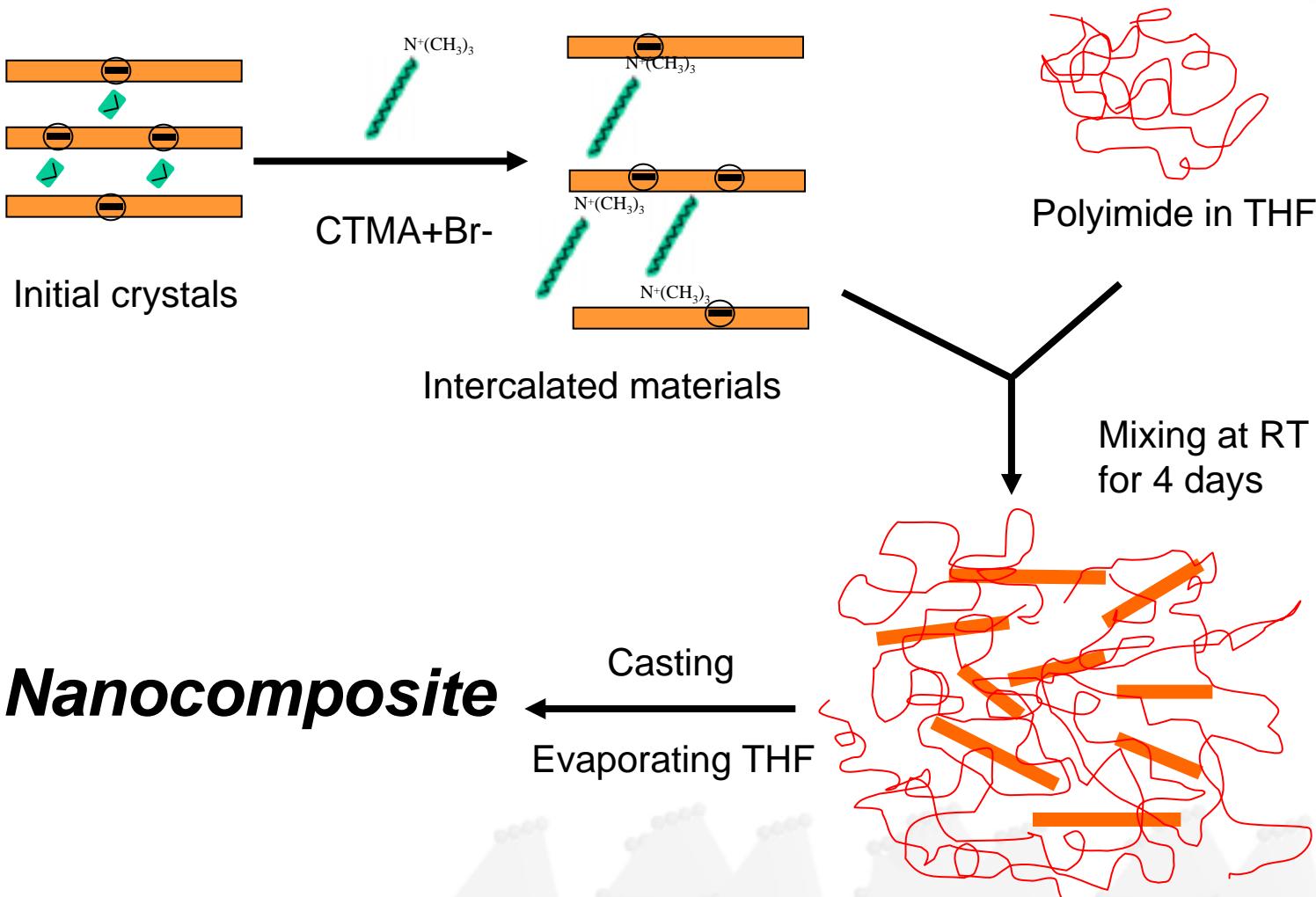


$$D = 9.4 \text{ \AA}$$

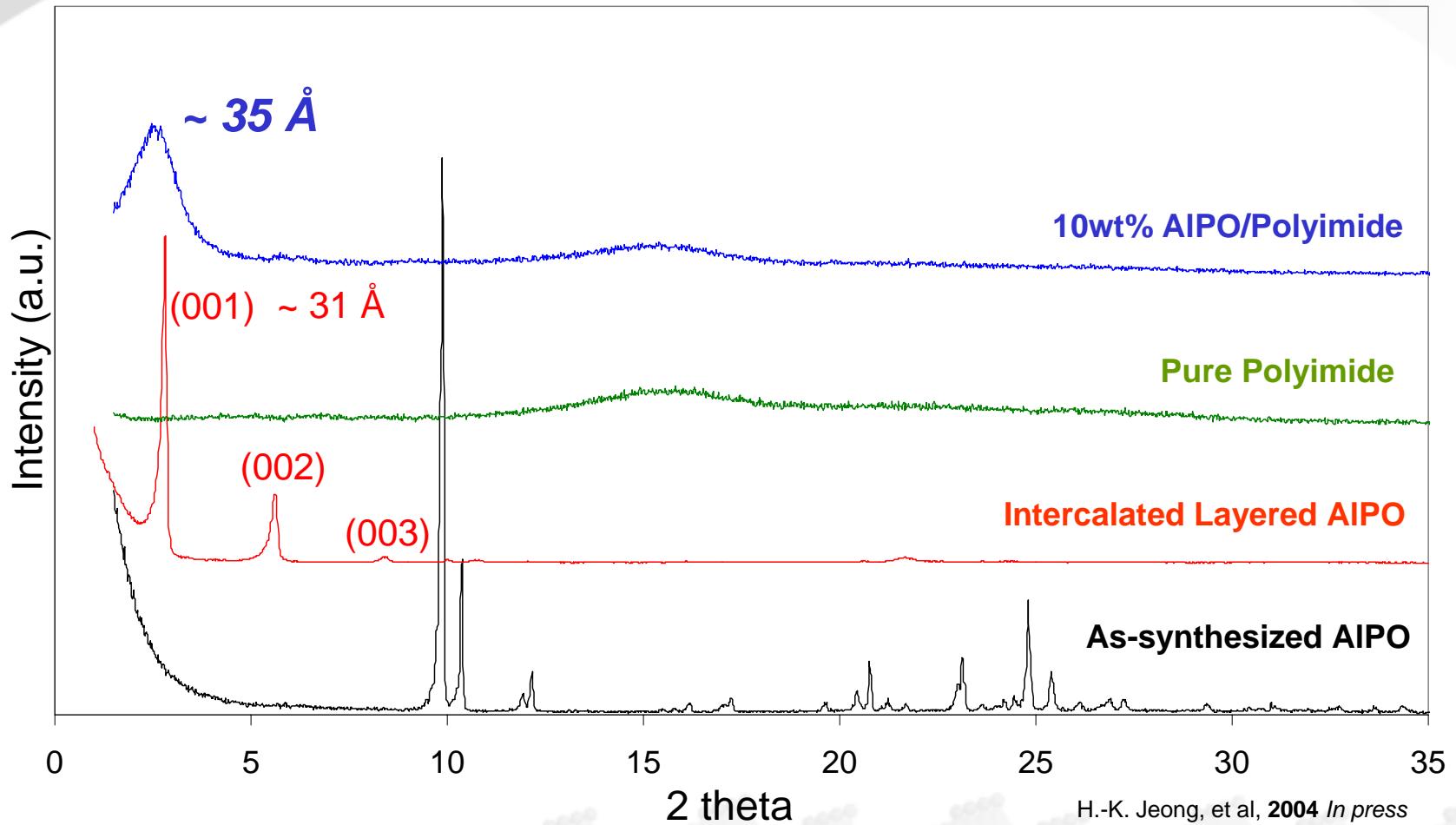
Green: Phosphorus
Purple: Aluminum
Red: Oxygen

Q.M. Gao, *J. Solid State Chem.*, 1997, 129, 37

Fabrication of Nanocomposite Membrane (In collaboration with Group of Eva Marand)

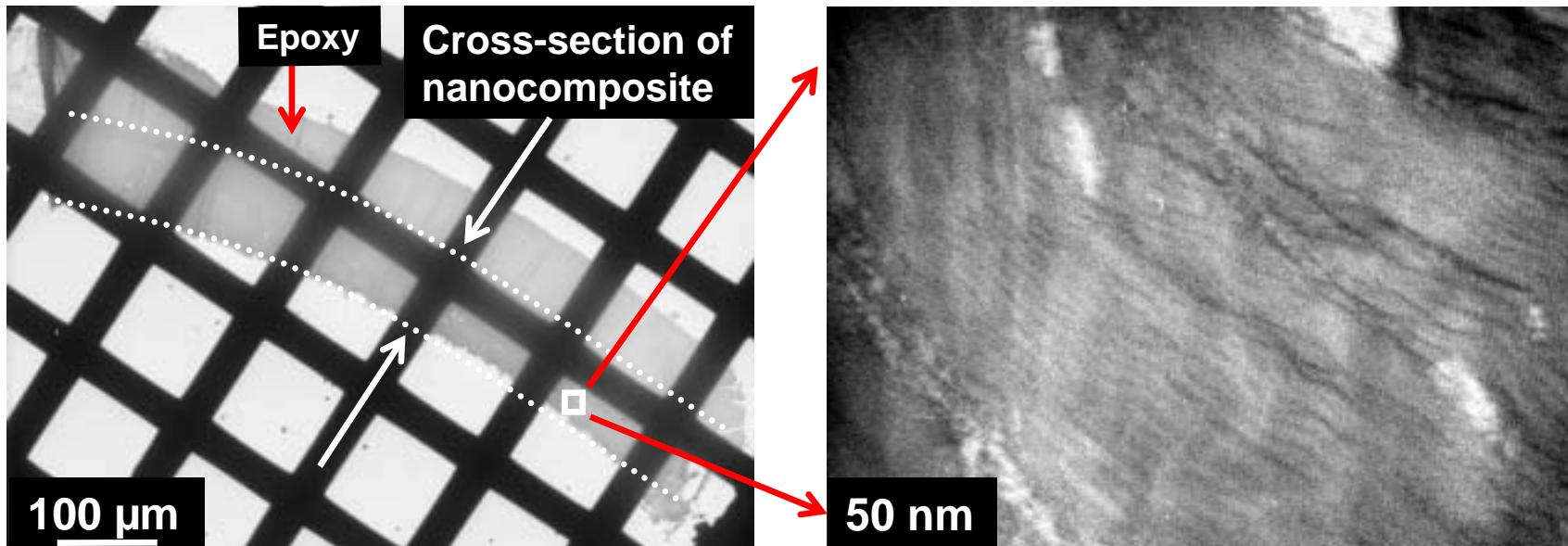


X-ray Diffraction Patterns



H.-K. Jeong, et al, 2004 *In press*

Transmission Electron Microscope Images

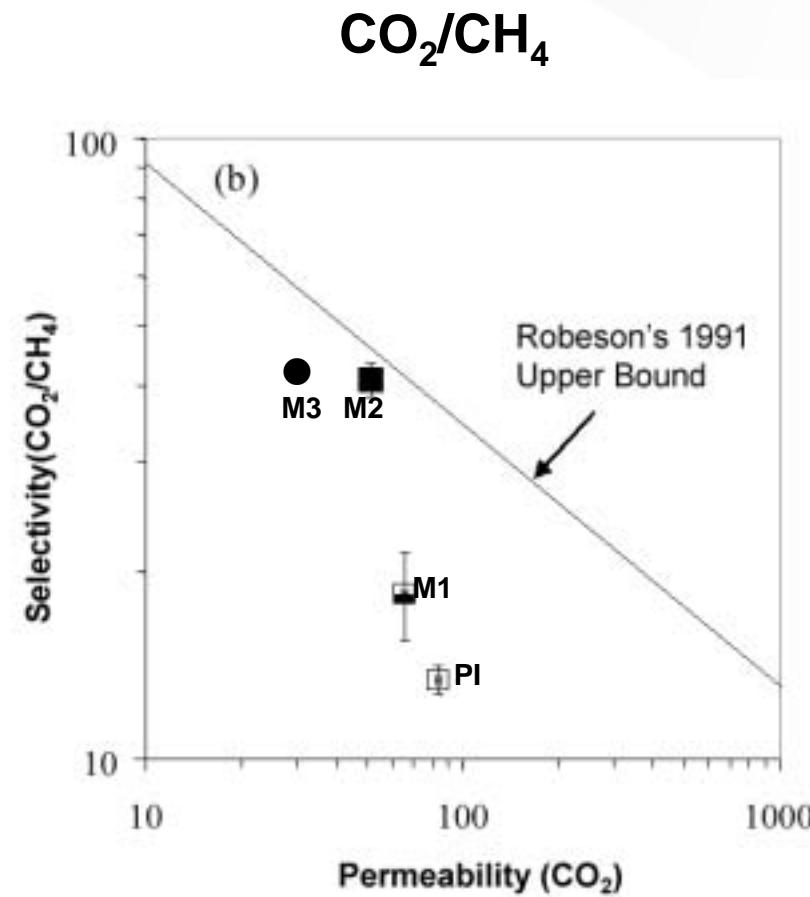
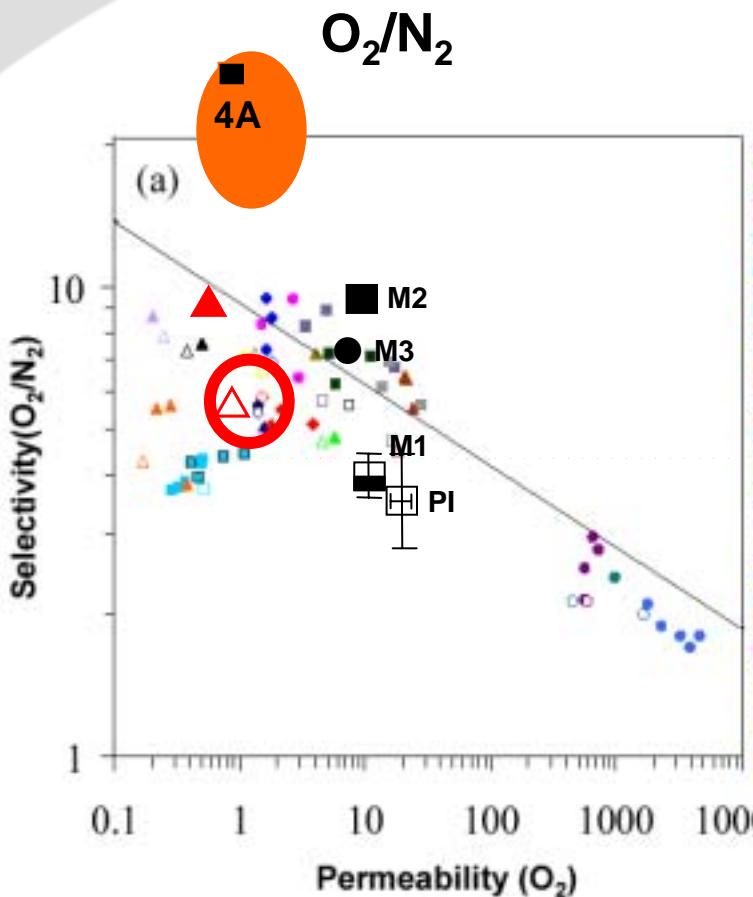


Inorganic domain $\sim 5 - 10 \text{ nm}$

Inter-domain Spacing $> \sim 10 \text{ nm}$

H.-K. Jeong, et al, 2004 *In Press*

Performance of Nanocomposite Membrane



□: Pure polyimide, ■: M1(5wt%), ■: M2(10wt%), and ●: M3(10wt%)

△: Matrimid

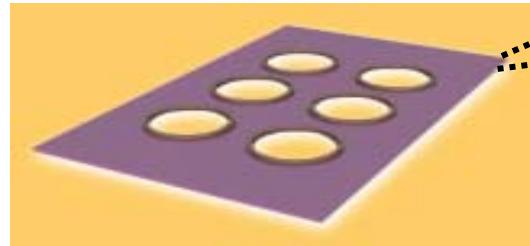
▲: 40wt% 4A/Matrimid

W. Koros, et al., *J. Appl. Poly. Sci.* 2002, 86, 881

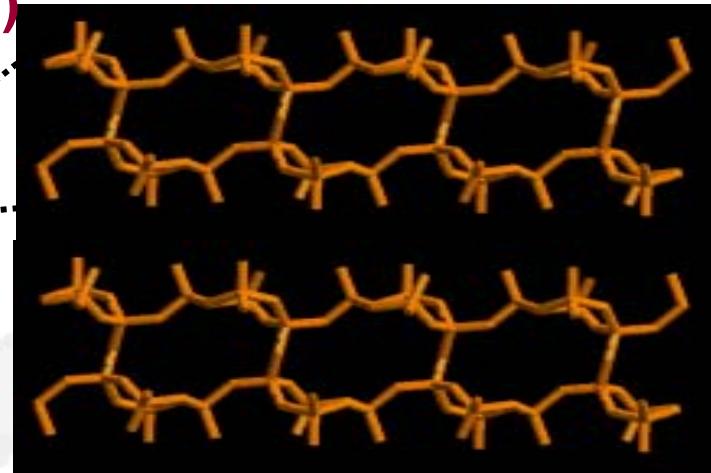
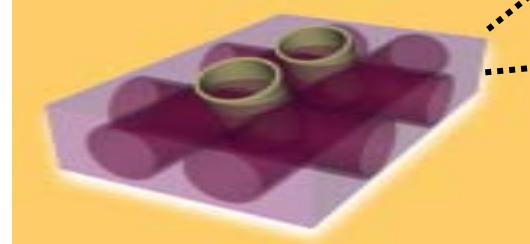
H.-K. Jeong, et al, 2004 *In Press*

Layered Material with Microporous Framework Layers

Layered Aluminophophates



Layered Silicate (AMH-3)



H.-K. Jeong, et al., *Nature Materials* 2003, 2, 53
H.-K. Jeong, et al., US patent USSN 60/391,988 (2002)



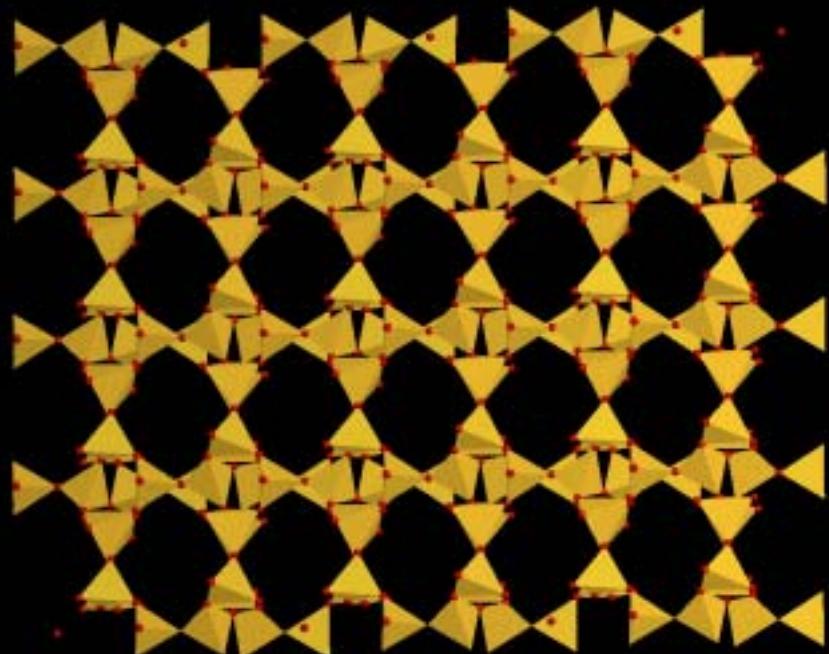
AMH-3, The First Layered Material with 3D Microporous layers

Microporous framework layers



projection along a-axis

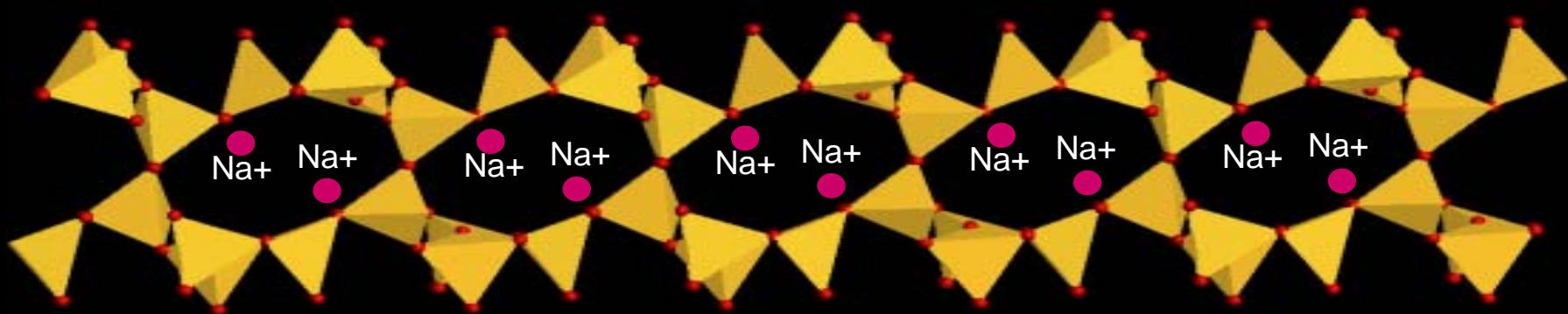
● : Na^+ ● : Sr^{2+} ● : O^{2-}



projection along c-axis

H.-K. Jeong, et al., *Nature Materials* **2003**, 2, 53
H.-K. Jeong, et al., US patent USSN 60/391,988 (2002)

Why Microporous Framework Layers ?



projection along a-axis

*Adsorption and Diffusion Properties
can be fine-tuned like Zeolites*

H.-K. Jeong, et al., *Nature Materials* **2003**, 2, 53
H.-K. Jeong, et al, US patent USSN 60/391,988 (2002)

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Polymer-Layer Nanocomposites

• H-K Jeong
W Kyrch (VPI with E Marand)

Collaborations:

• DG Vlachos (modeling of crystal growth), E Marand (polymer synthesis), Osamu Terasaki (HRTEM), Efrosini Kokkoli (AFM)

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